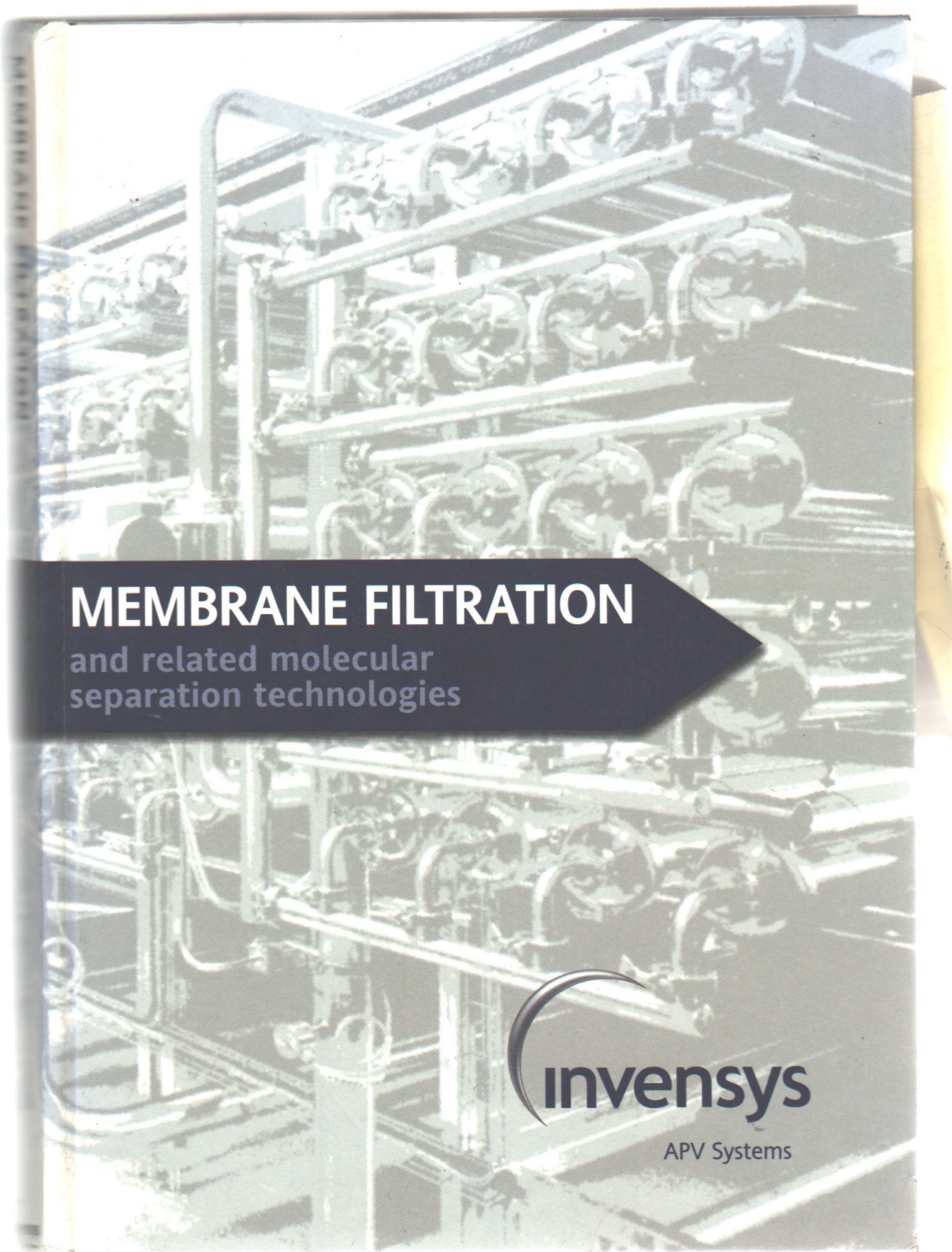

MEMBRANE FILTRATION

and related molecular separation technologies

invensys

APV Systems

Membrane filtration and related molecular separation technologies

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Foreword

This book is edited and published by APV Systems, an Invensys Group company.

APV has a long record in developing and supplying membrane filtration systems for customers worldwide. Originally serving the dairy industry, today's product programme covers a wide range of industries within the food, beverage, pharmaceutical and chemical sectors.

The intention of the book is to give customers, employees, students and others within 'the world of membrane filtration' a tool by which they can easily become acquainted with membrane filtration and a range of related molecular separation technologies.

In the book we have tried to reflect our position as an equipment manufacturer, making it as practically orientated as possible, including, however, a minimum of theoretical explanations sufficient for the reader to understand the processes and their potential industrial use. In this respect, the book can be seen as a complement to the more theoretically orientated literature on the subject.

The book is based on the experience of a range of people who have worked with membrane filtration since it was commercialised in the 1970s, and, as a further basis, available literature such as technical brochures, books, trade magazines, etc. have been used.

I would like to express my thanks to the many companies and institutions who have contributed with background information. Special thanks goes to Werner Kofod Nielsen, and the APV Membrane Filtration team. Whitout their efforts this book would not have been possible.

We hope that this book will be of use to you and serve as inspiration in whatever capacity you are working with the exciting technology of molecular separation processes.

Silkeborg, September 2000

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List of abbreviations

AC	alternating current
ATD	anti-telescoping device
BOD	biological oxygen demand
CA	cellulose acetate
CF	concentration factor
CIP	cleaning-in-place
CMC	carboxymethyl cellulose
COD	chemical oxygen demand
CP	concentration polarisation
CSEP	chromatographic separator
CTA	cellulosetriacetate
DF	diafiltration
DMF	dynamic membrane filter
ED	electrodialysis
EDR	electrodialysis reversal
EDTA	ethylenediaminetetra-acetic acid
EHEDG	European Hygienic Equipment Design Group
GS	gas separation
HF	hollow fibres
HFF	hollow fine fibres
IE	ion exchange
ISEP	ionic separator
IWP	isolated whey proteins
LC	liquid chromatography
LMH	litres/m^2 membrane area/hour
MF	microfiltration
MPC	milk protein concentrate
MSF	multi-stage flash distillation
MVR	mechanical vapour recompression (evaporator)
MW	molecular weight
NF	nanofiltration
NPN	non-protein nitrogen
P	permeability
PA	polyamide
PAN	polyacrylonitrile
PDMS	polydimethylsiloxane
PE	polyethylene
PES	polyethersulphone
PF	plate-and-frame
PLC	programmable logic controller
PP	polypropylene
ppb	parts per billion
ppm	parts per million
PS	polysulphone
PTFE	polytetrafluorethylene
PV	pervaporation
PVA	polyvinyl alcohol
PVC	polyvinylchloride
PVDF	polyvinylidenefluoride
QAE	quaternary aminoethyl anion exchange ligand
R	rejection
RFC	radial flow chromatography
RO	reverse osmosis
ROGA	reverse osmosis general atomic
SCE	Supercritical extraction
SCF	Supercritical fluids
SP	Sulphopropyl cation exchange ligand
SW	spiral-wound
TDS	total dissolved solids
3A	Symbol for the US Sanitary Standards Commitee under the DFISA (Dairy and Food Industry Supply Association)
TFC	thin film composite
TS	total solids
TVR	thermal vapour recompression (evaporator)
UF	ultrafiltration
UV	ultra violet light
USDA	United States Department of Agriculture
v/v	Volume per volume
VOC	volatile organic compound
w/w	weight per weight
WHO	World Health Organisation
WPC	whey protein concentrate
WPI	whey protein isolates

Introduction

This book is written to give readers who are not experts in separation technologies a tool with which to familiarise themselves with one of the most exciting developments during the past 25 to 40 years.

The industrial application of membranes was born from one single landmark event at the University of California, Los Angeles (UCLA) in 1960, when Loeb and Sourirajan developed the synthetic asymmetric cellulose acetate membrane. During this period, the US Office of Saline Water (OSW) was a part of the Department of the Interior, which heavily supported the development of processes to produce fresh water from the sea with alternative methods to distillation. One of the early participants in these research programmes was the Massachusetts Institute of Technology (MIT). Their work resulted in one of the first promising suggestions for ultrafiltration membranes and became the basis for the Amicon Corporation, a pioneer in commercialising membrane technology.

While the membrane business in the early 1960s was estimated to be worth less than USD 10 million, the total membrane business today is believed to be in the order of USD 1 billion, which is close to the estimated market for centrifugal separators and decanters of USD 1.2 billion in annual sales. Taking into consideration that mechanical separators have been around for 120 years, the figures for membrane filtration are quite impressive. In this context membrane filtration is used in its broadest sense including reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), electrodialysis (ED), gas separation membrane systems (GS) and pervaporation systems (PV).

Today RO, NF, UF and MF correspond to more than 60% (USD 600 million) of the total market of which RO and NF constitute approximately USD 240 million and UF and MF USD 360 million.

Membrane technology is applied in a wide variety of fields. Today desalination of sea and brackish water is normally done by RO, and plant sizes are in the million gallons per day range.

In the chemical industry, processes like electrocoat paint recovery, using UF, is one of the most successful uses of membrane technology.

Since the youth of membrane filtration, the dairy industry has been using membranes for a wide range of applications. The most illustrative application is that of whey separation and concentration, which has turned whey from being a large volume waste product, to being a raw material for very high value-added products such as high protein whey powder and isolated whey proteins. But this is just one example of a wide range of applications of membranes in the dairy industry, where membrane systems have become a natural part of dairy plants, as one of many unit operations on a par with separators and plate heat exchangers.

A similar situation applies in the pharmaceutical and health care industries, where fractionation of fermentation broth and high-performance membrane bioreactors for enzymatic and fermentation processes have become common technologies based on membrane filtration. This book will concentrate on the membrane filtration processes listed above.

Common to them all is a type of membrane, across which a driving force is applied to make the separation process happen. The separation takes place at the molecular level as in the separation of salt from sea water during water desalination with RO.

Separation at the molecular level is also the case for liquid chromatography (LC). The chromatography resin acts in many ways like the membrane material, except that it is particulate with an extremely large surface area, and is packed into a separation column.

In many cases, liquid chromatography and membrane filtration complement each other. LC provides excellent separation characteristics and can separate molecules which are quite close in size, charge and shape. This means that the cut-off value is much sharper than any membrane can provide, while membrane technology is usually less expensive in terms of investment and operating costs. In order to illustrate the synergies between such molecular separation processes, a review of LC, including ion exchange (IE), has been included.

After a description of the spectrum of separation processes and molecular separation, a chapter on the history of the various processes is presented.

This is followed by a description of each individual separation process, the membranes and resins, their chemistry, characteristics and manufacture.

Fluid dynamics and its importance for optimal operation of plants in terms of controlling concentration polarisation and reducing fouling is the subject of a separate chapter, followed by a brief introduction to the theory of transport mechanisms through membranes. The following chapter describes each membrane system in terms of the variety in membrane configuration.

The different types of resin-based systems, including both ion exchange and chromatography, are covered in separate chapters.

The correct design of process plants is crucial for successful industrial utilisation of all molecular separation processes, and the basic process design criteria are also covered.

Lab systems are necessary for the successful exploitation of the various processes. In many cases, an application may be tried for the first time, or a new membrane may be tested on a known application, and the result compared with the membrane type normally used. Some of the most common pilot systems are reviewed.

The application of molecular separation processes is continuously growing, and this book covers some of the most interesting and important applications from the point of view of industrial utilisation.

The chapter on economics gives some guidelines to the cost of investment and operation of some plant types, followed by examples illustrating how a comparison with other processes may be made. It should always be kept in mind that in most cases processing economy is the determining factor for whether or not the technical solution is carried through in real life. Moreover, some examples are given of how to calculate processing costs and how such costs can be compared with the costs of alternative processes.

Intelligent combinations of various types of separation processes will probably become more common in the future. This may not necessarily be limited to molecular separation processes but could also include other processes.

Finally the last chapter looks into the future. What will the next decades bring? Has the excitement gone? Has the consolidation phase been reached?

1 Separation technologies

When two or more substances in a solution are separated into their individual components, a separation process occurs. In its most simple form, the formation of a cream layer on non-homogenised milk directly from the cow is a separation process driven by gravity in that the fat globules in the cream are lighter than the liquid phase of the milk. Many food products, cleaning agents and other household products have to be shaken before use. This is because a separation process has taken place and needs to be reversed prior to use of the product.

There is a wide range of separation processes, and each process is associated with a particular technology and equipment. In order to facilitate the understanding of the nature of these technologies and the role each of them plays, they may be categorised into 'families' as shown in Figure 1.

Mechanical separation by gravity
- Sedimentation
- Flotation

Conventional filtration (dead-end)

Mechanical separation by centrifugal force
- Separators and decanters
- Hydrocyclones

Separation by phase change
- Evaporation
- Drying
- Crystallisation
- Distillation

Separation by extraction
- Liquid - liquid
- Solid - liquid
- Supercritical (SCE)

Separation by adsorption
- Activated carbon

Molecular separation
- Reverse osmosis (RO)
- Nanofiltration (NF)
- Ultrafiltration (UF)
- Microfiltration (MF) *(cross-flow)*
- Dialysis
- Electrodialysis
- Gas separation
- Pervaporation
- Chromatography
- Ion exchange

Figure 1: The family of separation processes.

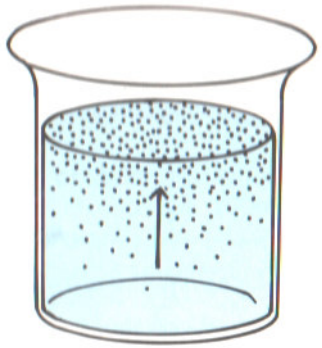
Mechanical separation by gravity

Mechanical separation by gravity is the most simple form of separation. A coffee filter used for extracting coffee from coffee beans with boiling water is a good example from our daily lives.

In a *sedimentation process*, particles in a liquid, when left standing, will precipitate to the bottom, provided the difference in density between liquid and particles is sufficiently large.

In the *flotation process*, the particles float to the top layer of the liquid similarly to when cream is separated from non-homogenised milk. In order to facilitate the flotation process, flocculents may be added and air injected at the bottom of the separation vessel. The top layer, typically containing fat and proteins, may be removed continuously or batch-wise.

Natural sedimentation



Stoke's law:

$$v_g = \frac{d^2 (\rho_p - \rho_l)}{18\eta} \times g$$

where

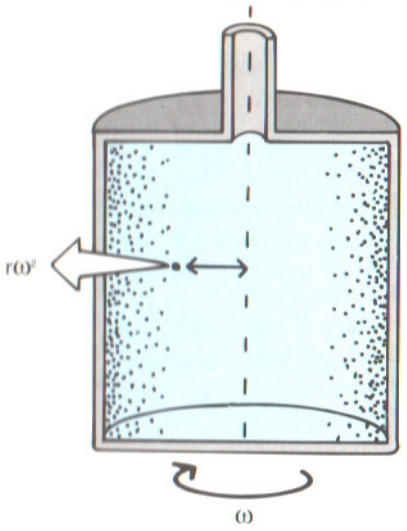
v_g	=	velocity of particle/gravity	m/s
d	=	particle diameter in	m
ρ_p	=	particle density in	kg/m^3
ρ_l	=	density of liquid phase in	kg/m^3
η	=	viscosity of liquid phase in	kg/ms
g	=	gravitational attraction of the earth 9.81	m/s^2

For a fat globule in milk with
d = 3µm, ρ_p = 980 kg/m^3, ρ_l = 1028 kg/m^3 and
η = 1.42 centipoise

$$v_g = -0.6 \text{ mm/h}$$

This means the fat globule will rise to the surface (flotation) but at a very low velocity

Centrifugal separation



a	=	$r \times \omega^2$	
v_c	=	velocity/centrifugal force	m/s
a	=	acceleration in	m/s^2
r	=	radius to particle in	m
ω	=	angular velocity in	revolutions/s

$$v_c = \frac{d^2 (\rho_p - \rho_l)}{18\eta} \times (r \times \omega^2)$$

$$\omega = \frac{2 \times \pi \times n}{60}, \quad n = \text{revolutions/minute}$$

With the same data for a fat globule as stated above and n = 4500 rpm at a radial position of 0.2 m

$$v_c = -0.75 \text{ mm/s}$$

which is almost 4500 times (0.75/0.6 × 3600) greater than for natural sedimentation

Conventional filtration

In *conventional filters*, the gravity may be enforced by using a pump to create a pressure which will speed up the rate of filtration. Due to the formation of a filter cake, the rate of filtration may quickly slow down again, which necessitates removal of the filter cake or back-flushing of the filter in order to re-establish the capacity. The filtration rate may also be increased by the use of vacuum as in vacuum drum filters. In this case, the filter cake is removed continuously by a knife scraping off the solids at a certain level on the rotating drum.

In some cases the rate of filtration can be improved by using a filter aid which is added to the liquid prior to filtration. Kieselguhr is a well-known filter aid which is used, for instance, in the brewing industry.

Mechanical separation by centrifugal force

Natural sedimentation by gravity is limited even though pressure and vacuum can assist in increasing separation velocity.

About 100 years ago, Gustaf de Laval introduced the centrifugal separator, equipped with conical discs, which was originally patented by Freiherr von Bechtolsheim in Germany, and had been acquired in 1889 by the Swedish company AB Separator, of which Gustaf de Laval was part-owner. In the centrifugal separator, the velocity is increased several thousand times compared with natural sedimentation or flotation. A field of centrifugal force is generated by spinning a vessel filled with liquid. This creates a centrifugal acceleration which is not constant like the gravity in a stationary vessel. Centrifugal acceleration increases with distance from the axis of rotation and with the speed of rotation expressed as angular velocity.

Natural sedimentation governed by Stoke's law is compared to centrifugal separation in Figure 2, where it is demonstrated that the sedimentation velocity in a centrifugal separator rotating at 4,500 rpm is approximately 4,500 times greater than that of conventional gravity sedimentation.

Centrifugal separators can be built as clarifiers or separators depending on the design of the disc stack. Clarifiers remove particles and impurities with a larger density than the liquid phase, whereas separators divide the liquid into three phases as for skimming and purification of milk. A special separator design is required for removal of micro-organisms.

Decanter centrifuges are used for continuous sedimentation of suspended solids from a liquid by the action of centrifugal force. The decanter is an elongated, horizontal rotating bowl equipped with an axial screw conveyor for continuous unloading of separated solids from the rotor. The decanter handles very high solid levels as in production of lactose and casein or in treatment of sludge from municipal waste purification plants.

In hydrocyclones the centrifugal force is also utilised to accelerate the rate of separation. A typical hydrocyclone includes an elongated, conical separation chamber of circular cross section which generally decreases in cross sectional area from a large end to a small or apex end. An outlet for the more dense components is provided at the apex of the conically shaped separating chamber, while the less dense components of the feed stream exit through an overflow outlet at the opposite end of the conical chamber. Even though the rate of separation is greatly improved compared with ordinary gravity separation, it is still not nearly as high as in centrifugal separators. The cost, however, is much smaller since hydrocyclones are stationary without any rotating parts. The most successful applications are in oil/water separation on off-shore oil drilling platforms.

Separation by phase change

In *evaporation* and *drying*, a solvent, in most cases water, is removed from a solution. In the evaporation process, most of the moisture will be removed, and removal of residual moisture, if necessary, will take place in a dryer. In both cases the solvent is evaporated, removed, and condensed. This requires that the heat of evaporation is added, which makes these processes very energy-consuming.

In evaporation, it is possible to reuse the heating medium after regeneration via

electricity or high pressure steam. There is a large number of evaporator types known as falling film, rising film and forced circulation evaporators. The most common heat transfer devices are tubular or plate evaporators. In dryers, the solvent is usually removed by hot air as vapour. Spray dryers, fluid bed dryers, spin flash dryers and drum dryers reflect some of the most common drying devices. Heat recovery systems are essential to improve operating economy.

Water can also be removed by *crystallisation*, i.e. freezing the water to ice crystals and subsequently removing the crystals. This has been proposed for making drinking water from sea water and it is known from the food industry, e.g. in freeze drying of coffee. The fact that the process takes place at a very low temperature means that the construction materials are exposed to a more gentle environment in respect of corrosion and wear, but most importantly, it means that the products are much improved in quality.

Another common application of crystallisation is in the sugar industry for production of crystalline sugar from sugar juice. After the purified sugar juice has been concentrated in a multi-stage evaporator, more water is removed in a boiling pan, which is a large batch cooker. When the solution is sufficiently saturated, it is seeded with very fine, ground sugar which forms a large number of sugar crystals which subsequently grow to the specified size. The sugar crystals are separated from the surrounding sugar syrup in a centrifuge and washed in the centrifuge with a sugar solution and water.

Crystallisation is also used in production of lactose from raw whey or from whey in which the proteins have been removed by UF.

Distillation is used for separation of mixtures containing two or more volatile components. It is used for solvent recovery, aroma recovery, low-alcohol beer production, and azeotropic distillation, to mention but a few applications. It is the most common unit operation in the oil refinery industry. Since the process is based on evaporation of the components, it consumes a lot of energy.

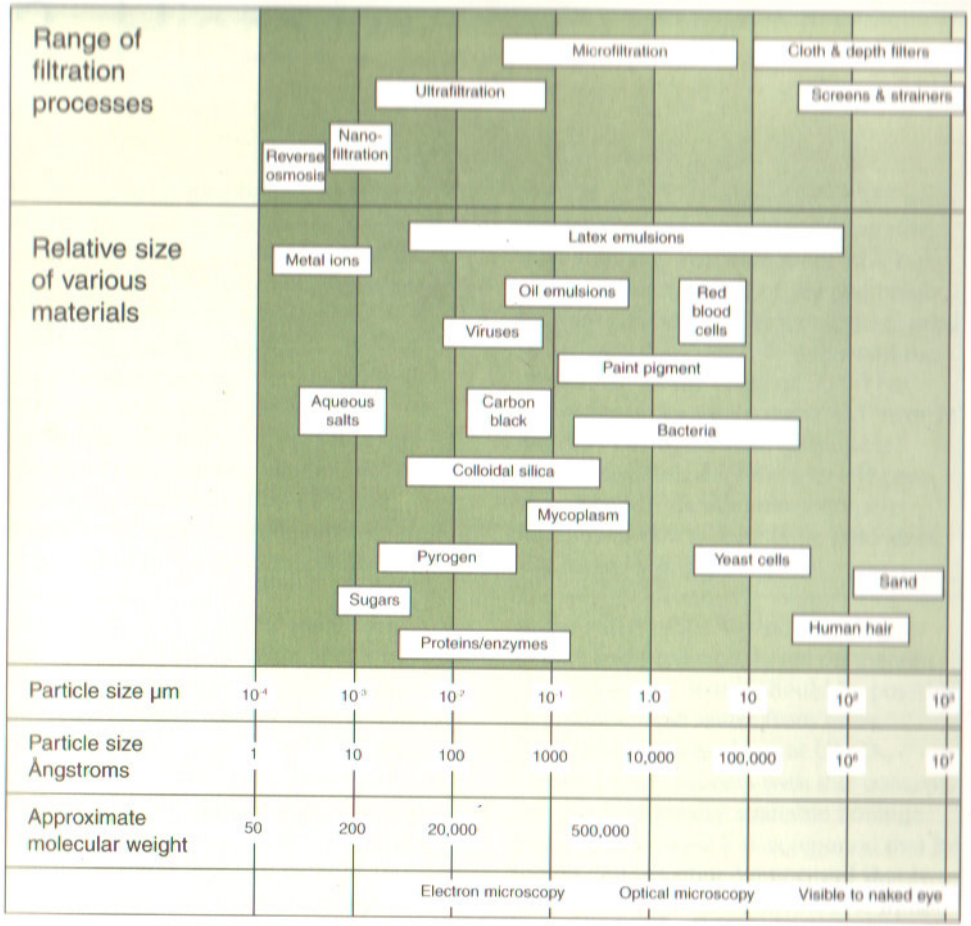
Separation by extraction

Extraction is the removal of soluble components from solid or liquid materials by means of an immiscible solvent. It is classified into liquid-liquid, solid-liquid, and supercritical fluid extraction. In its simplest form, brewing of tea and coffee is achieved through extraction. One of the first industrial applications was extraction of sugar from sugar beets, which is the basis for the entire beet sugar industry. Extraction is used widely in the pharmaceutical and health care industries, e.g. for extraction of insulin from fermentation broth.

Supercritical extraction (SCE) is based on using supercritical fluids (SCF) such as carbon dioxide under very high pressure. Such processes are more environmentally friendly than conventional extraction processes, where solvents like hexane, propane and chlorinated hydrocarbons are used, and consequently better suited for the food industry. Removal of caffeine from coffee beans for production of decaffeinated coffee is a typical application, and it has also been proposed to use SCE for removal of cholesterol from butter fat.

Separation by adsorption

Small quantities of organic compounds can be removed by means of activated carbon. This process may also be used to remove chlorine and chlorinated organic compounds from drinking water, or traces of organic colour compounds in food manufacturing.



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As already mentioned, this book will concentrate on *molecular separation processes*, but frequent comparisons will be made to other separation processes which are sometimes competing and sometimes complementary. In many cases, some of the other processes are used for pre-treatment of liquids prior to a membrane system.

The term 'dead-end filtration' is sometimes used to distinguish conventional filtration from cross-flow filtration where systems are designed to provide a high velocity across the filtration media to prevent build-up of a filter cake. Theoretically, all membrane filtration processes can be characterised as cross-flow filtration processes, but the term is primarily used to describe MF and UF. MF, however, may be used both as a dead-end filtration and a cross-flow filtration process depending on the applications.

Another way of characterising the range of separation processes is the *Filtration Spectrum* as illustrated in Figure 3.

2 History

For many years membrane processes, separating molecules and ions, were regarded as processes of interest in the laboratory only because the membrane throughput was too small to be of interest in industrial applications. However, there are reports from as early as 1863 that dialysis membranes were used in the sugar industry for salt removal from molasses. The membranes at that time were made from hog's bladder, parchment paper or copper ferro-cyanide, precipitated in the pores of porcelain.

In 1865 the first synthetic membrane based on nitrocellulose was prepared. The first quantitative measurements of diffusion phenomena and osmotic pressure were made, using these early membranes. At this time, membranes made of collodion - a term used for polymers based on cellulose - became known and created an opportunity to manufacture artificial kidneys. The manufacturing procedure was to dissolve nitrocellulose in a suitable solvent, such as alcohol-ether or acetic acid, and pour the solution on a flat surface, allowing the solvent to evaporate. Around 1907 a method for controlling the pore size in collodion membranes was developed by controlling the rate of evaporation of the solvents and by water washing of the film.

Membrane filters became commercially available as early as in 1927 from the Sartorius company in Germany. Until 1945 membrane filters were used primarily for removal of micro-organisms and particles from liquid and gaseous streams, for diffusion studies and for sizing of macro-molecules. In 1957 the US Public Health Service officially adopted the membrane filtration procedure for drinking water analysis.

Parallel to this development of MF membranes, there was considerable interest in developing membranes for RO, especially for desalination of sea and brackish water. However, the membranes used so far were too fragile to withstand the pressures – in the order of 30-80 bar – necessary to desalinate water and 'reverse' the flow through a semi-permeable membrane caused by the osmotic pressure. The MF membranes were also unsuitable, due to their large pore sizes and inability to reject salt.

In the early 1950s Yuster, working at UCLA had predicted, based on theoretical evaluations, that it should be possible to produce fresh water from brine. Sourirajan, also working at ULCA, reported some success with this concept, using commercially available homogeneous membranes. It was reported that he used a hand-operated pump and that it took a few days to produce a few millilitres of fresh water. The conclusion of most researchers at this time was to reduce the thickness of the membrane to obtain a feasible flux rate. Sourirajan, now joined by Loeb at UCLA, attempted to modify commercially available cellulose acetate membranes by heating them under water to open the pore structure in order to increase flux rates.
Unfortunately exactly the opposite happened: the membrane structure shrank and became denser. As a next step they tried to take commercially available open UF cellulose acetate membranes and heat them under water. This caused the pores to shrink, giving improved salt rejection, and simultaneously the flux increased to higher values than ever seen before. This is illustrated in Table 1, which shows that the flux rate from the original tests in 1958 by Yuster was increased by a factor of almost 300.

Researcher	Morphology	Applied pressure bar	Flux rate lmh**	Rejection of NaCl %
Breton, 1957	Homogeneous	?	?	99+
Yuster et al., 1958	Homogeneous commercial	57	0.05	94
Loeb and Sourirajan, 1963	Asymmetric commercial	78	3.0	92
Loeb and Sourirajan, 1963	Asymmetric*	75	14.5	99

* The Loeb - Sourirajan membrane
** Litres per square metre per hour

The structure of the Loeb-Sourirajan membrane is characterised by a very thin 'skin' on the surface usually only 0.1-0.2 µm, whereas the main body of the membrane is 'sponge like' with extremely porous voids. Since the total thickness of a membrane is in the order of 100-200 µm, the surface layer only constitutes approximately 0.1% of the entire membrane. The surface layer determines salt rejection and flux rate and the substructure provides the mechanical strength of the membrane.

Figure 4 shows a cross section of an asymmetric membrane.

Parallel to the development of membranes, the development of systems evolved, and it was during these years that the foundation was laid for hollow fibres (Amicon), hollow fine fibres (DuPont), spiral-wound (Gulf General Atomics), plate-and-frame (Aerojet General), tubes (Havens), and leaf (Dorr Oliver). DDS (The Danish Sugar Corporation) took up the development of the plate-and-frame system in the late 1960s.

Altogether, 1960-1975 was a flamboyant period in the history of membrane filtration where everything happened and everything seemed possible. A great deal of R&D was initiated, and several commercial corporations were founded in this period. Following the development of membranes and systems, came a very interesting period of application development. Water treatment, electrocoat paint recovery, whey treatment and enzyme recovery were the most interesting and promising applications.

The next milestone was the launch of the thin film composite membrane (TFC) making it possible to manufacture desalination membranes from non-cellulosic material, and, at the same time, separately tailor the support structure of the membrane and the active thin film layer. This resulted in membranes with greatly improved performance in respect of flux rate and rejection of salt, while at the same time the resistance to temperature and chemicals was significantly improved. This made it possible to provide better and safer cleaning of membrane systems.

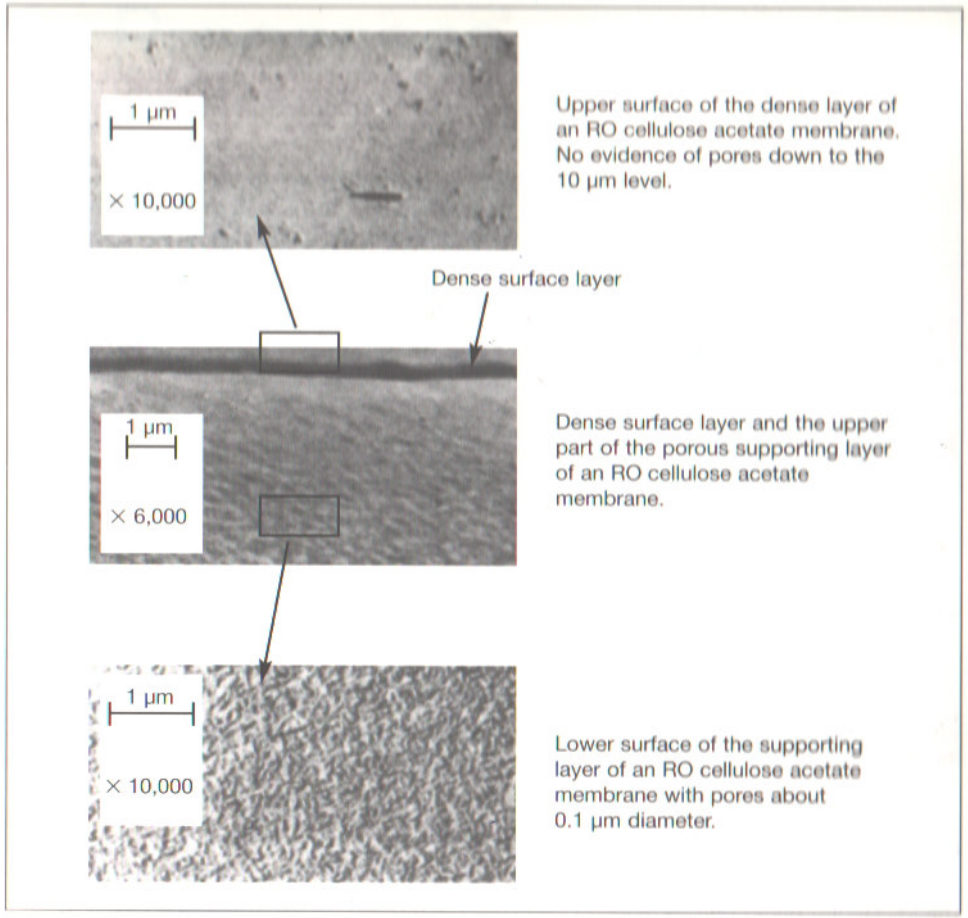

Photo: Riley, Merten, Gardner

Figure 4: The Loeb Souriraja asymmet membrar A cross s of an asymmet cellulose acetate membrar showing porous substruct covered very thin, top layer.

Film Tec Corporation, which was initially started on the basis of a research group from North Star Research Institute in Minneapolis, launched the FT range of membranes in 1981. Here the support membrane was made from polysulphone cast on a strong, non-woven support paper of polyester. The thin film composite layer was manufactured in situ from monomers forming a polyamide with outstanding salt rejection properties.

Inorganic membranes (mineral or ceramic membranes) became known in the mid-1980s, through companies like Union Carbide in the USA and SFEC (Societé de Fabrication d'Elements Catalytiques) in France. The membranes were initially manufactured from porous carbon tubes covered with an active layer of zirconium oxide. Later on, Ceravèr (France) launched the ceramic membranes based on aluminia oxide. The ceramic membranes had outstanding temperature and chemical resistance and were predicted to last forever, but their original performance was fairly poor. However this was improved, and today ceramic membranes are the basis for most cross-flow MF operations.

3 Processes

Process	Driving force	
Reverse osmosis	Pressure difference	(ΔP)
Nanofiltration	Pressure difference	(ΔP)
Ultrafiltration	Pressure difference	(ΔP)
Microfiltration	Pressure difference	(ΔP)
Dialysis	Concentration difference	(ΔC)
Electrodialysis	Electrodialysis Electr. Pot.	(ΔE)
Gas separation	Pressure difference	(ΔP)
Pervaporation	Concentration difference	(ΔC)
Ion exchange	Ionic charge/size	
Chromatography	Adsorption/non specific	
	Ionic strength/electrostatic interaction	
	Gel permeation/molecular sieve	
	Affinity/biospecific sorption	

Figure 5: The key parameters influencing the velocity of different separation processes.

This chapter describes the various molecular separation processes referred to in Figure 1. The processes fall into different categories as illustrated in Figure 5.

Membrane filtration

The term *membrane filtration* is generally accepted as the common denominator for reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF).

Membrane filtration processes are characterised by their capability of separating molecules of different sizes and characteristics. RO is based on a very dense membrane, rejecting virtually all soluble substances except water. In order to overcome the osmotic pressure, the operating pressure is relatively high.
The principle of RO is illustrated in Figure 6.

NF is basically a special version of RO in which the membrane is slightly more open in structure, allowing mainly small ions like sodium and chloride to pass, and rejecting larger ions and most organic components. The operating pressure is below what is required for RO, since the osmotic pressure difference to overcome is smaller. The principle of NF is illustrated in Figure 7.

In UF, the membrane is more open in structure and typically allows salts, sugars, organic acids and smaller peptides to pass, while proteins, fat and polysaccharides are rejected. The pressure is fairly low compared with RO and NF. UF is a combined separation and concentration process. The principle of UF is illustrated in Figure 8.

Finally, MF is based on a membrane with a very open structure allowing most dissolved substances to pass, while non-

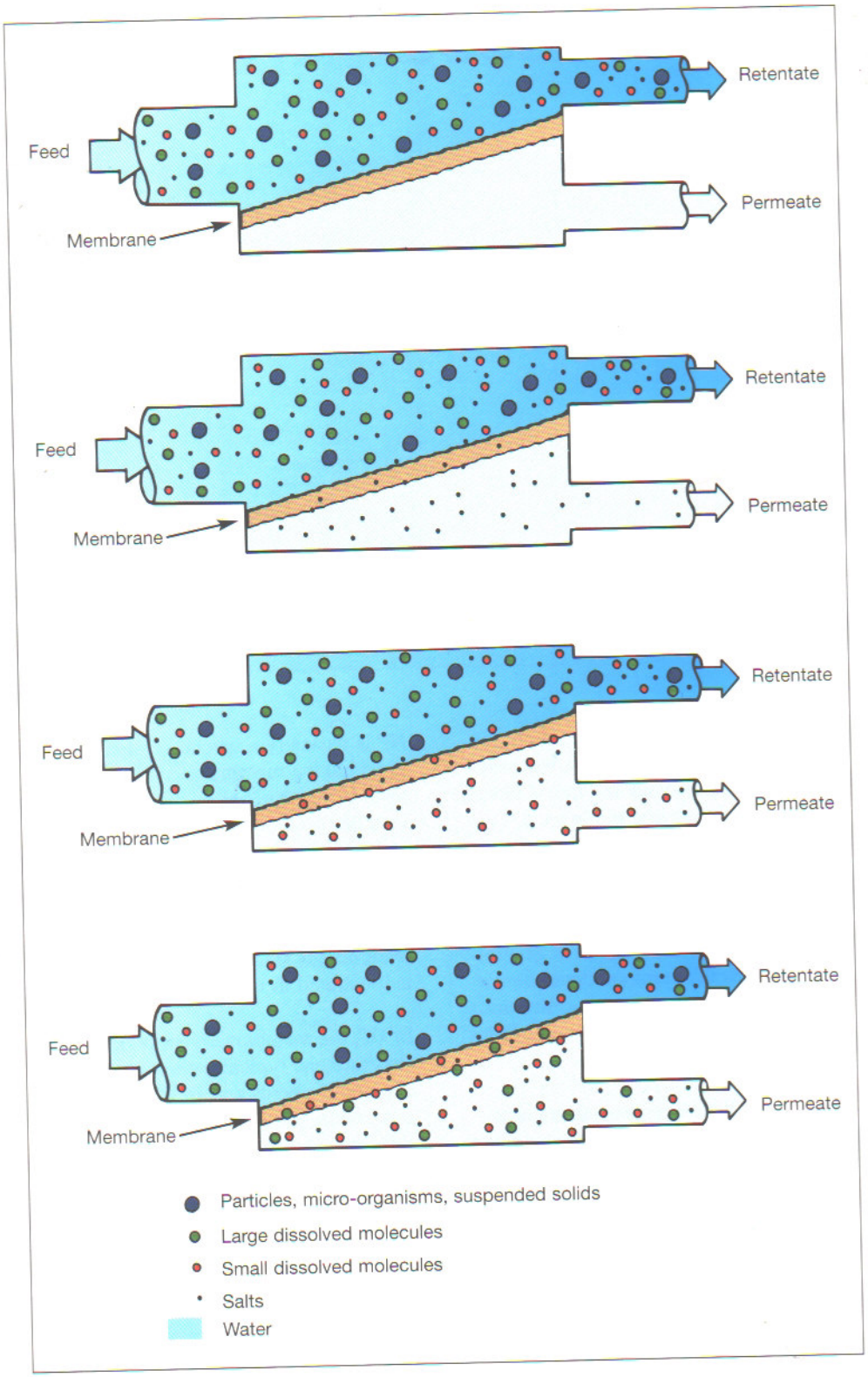

Figure 6: Reverse osmosis.

Figure 7: Nanofiltration.

Figure 8: Ultrafiltration.

Figure 9: Microfiltration.

Process	Membrane pore size µm	Common trans-membrane pressure range bar	Major limiting factors
Reverse osmosis	10^{-4}-10^{-3}	30-80	Osmotic pressure
Nanofiltration	10^{-3}-10^{-2}	20-35	Osmotic pressure
Ultrafiltration	10^{-2}-10^{-1}	1-10	Gel formation/ concentration polarisation Retentate viscosity
Microfiltration	10^{-1}-10^{1}	<1	Trans-membrane pressure control pore plugging

Table 2: Comparison of membrane filtration processes.

dissolved particles, bacteria and fat globules are rejected. The principle of MF is illustrated in Figure 9.

Table 2 illustrates how the pore sizes increase from RO to MF. The trans-membrane pressure (pressure difference over the membrane) is decisive for plant design and choice of components, and varies from less than 1 bar for MF to 80 bar or sometimes even as high as 100 bar for RO.

Reverse osmosis

When two liquids are separated by a semi-permeable membrane as shown in Figure 10, water will flow through the membrane to create the same chemical potential on both sides of the membrane. Since the salt is unable to pass the membrane pores, the water flowing through the membrane will try to equalise concentrations in the two vessels. The solution will rise to a level where the height of the column results in a pressure equal to the osmotic pressure. If a pressure is applied to the column, the flow of water will be reversed, and when the pressure exceeds the osmotic pressure pure, water will pass from the concentrated to the

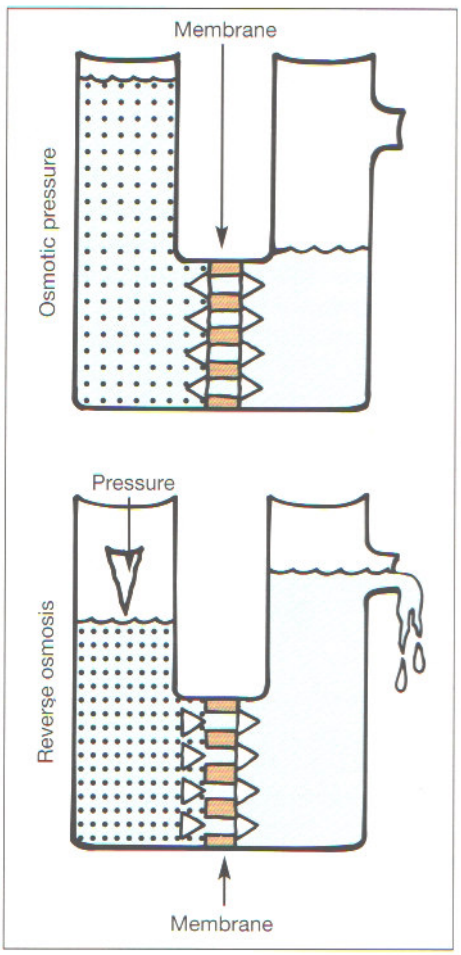

Figure 10: Reverse osmosis. Pressure is used to reverse the osmotic flow.

less concentrated solution. This is called reverse osmosis.

The osmotic pressure is obviously a key factor since it determines the capacity of a membrane at a given pressure. The osmotic pressure (π) can be determined from the van't Hoff equation:

$$\pi = n \times R \times T$$
$$\pi = C \times R \times T / M$$

where

n = molar concentration of solute in moles/litre
C = concentration of solute in g/litre of solution
M = molecular weight of solute
T = absolute temperature in °K
R = gas constant

This illustrates the fact that the osmotic pressure for a given concentration increases as the molecular weight decreases. Table 3 shows the osmotic pressure for a range of solutions and for different types of products.

Table 3: Osmotic pressure in different products.

Product	Total solids %	Osmotic pressure bar
Casein	3.5	0.03
Lactose	5.0	4.1
Milk	11	7.0
Whey	6	7.0
Orange juice	11	16.2
Apple juice	14	21.1
Grape juice	16	21.1
Sea water	3.5	24.6
Coffee extract	28	35.2

In brief, RO is a process in which the osmotic flow is reversed by applying a pressure to the liquid in excess of the osmotic pressure difference across the semi-permeable membrane separating two liquids with different osmotic pressures. In some literature this is called *hyperfiltration* so as to match the terms nano-, ultra- and microfiltration. This book will continue to use the term *reverse osmosis*.

The semi-permeable membrane is usually not perfect and will not provide a 100% separation. In the characterisation of membranes, the terms *flux rate* and *salt rejection* are commonly used.

The membrane pore size is smaller than 2 µm and not detectable by the pore size characterisation methods available today. Also, because diffusion becomes very important in high-retention RO membranes, it does not make sense to talk about pores any longer, and sometimes the term *equivalent pore diameter* is used.

Chapter 6 will go into details with the transport properties of membranes, but already at this stage it is useful to know the following simple equations:

$$J_w = A (\Delta P - \Delta \pi)$$
$$J_s = B \times \Delta C$$

where A and B are temperature dependent constants and

J_w = solvent flux (mostly water)
ΔP = hydrostatic pressure difference
$\Delta \pi$ = osmotic pressure difference
J_s = solute flux
ΔC = concentration difference

This means that the solvent flux is proportional to the difference between the absolute pressure difference and the osmotic pressure difference, while the solute flux is proportional to the concentration difference. The equations show

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$R = (1 - c_p/c_f) \times 10$

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R = salt rejection in
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that the water flux increases as pressure increases, but only after having surpassed the osmotic pressure difference. Since pressure increases the water flux but has no influence on the salt flux, the salt rejection will increase with increasing pressure. The salt rejection is defined as:

$$R = (1 - c_p/c_f) \times 100$$

where

R = salt rejection in percent
c_f = concentration of solute in feed
c_p = concentration of solute in permeate

Hardly any membrane can perform a 100% separation of water and salt, but today it is possible to achieve a salt rejection of more than 99%, which makes it possible to desalinate sea water to below 500 ppm salt in the permeate, which is the maximum quantity in drinking water allowed by WHO. Lower molecular weight components such as lactic acid, urea and other organic compounds generally have a lower rejection rate which may cause high BOD levels in the permeate, depending on pH, concentration degree, etc. This becomes an issue when organic products like juice, milk, whey and beer are concentrated.

RO is used to concentrate liquids with low solids levels and can replace evaporation until the point where the osmotic pressure becomes a limitation. The energy requirement is much lower since the water does not need to be evaporated and condensed. RO is also much gentler to the product, which in many cases will result in an improved product quality.

Nanofiltration

NF is an RO process with a relatively open membrane structure allowing in particular small monovalent ions such as sodium and chloride to pass through the membrane.

Property		Type 1	Type 2
Lactose rejection	%	99	96
$MgSO_4$ rejection	%	98	96
NaCl rejection	%	50	27
Water flux	lmh	54	73

Data measured at 10 bar and 25° C

Table 4: Performance data for nanofiltration membranes.

The process uses pressure as the driving force, but unlike RO, the pressure is usually kept relatively low (20-30 bar) in order to reduce salt rejection as much as possible and reject molecules with molecular weights in the order of 200 and above. Since low molecular weight salts pass through the membrane, the osmotic pressure difference across the membrane is reduced, which also contributes to a reduction in operating pressure.

NF membranes are usually of the thin film composite *type* where it is possible to tailor the structure of the surface layer to achieve their special characteristics. Table 4 shows some typical data for two types of NF membranes.

The NF process has a wide range of applications in the food, dairy, pharmaceutical and health care industries. Demineralisation of whey, milk and permeate from UF of milk and whey are major applications, as are concentration of sugar, protein and recovery of enzymes.

The capability of removing minerals, especially sodium chloride, without losing major organic compounds and simultaneously removing water and concentrate, makes the NF process quite unique and opens up a large range of possible new applications. In the environmental sector the process is used to purify and reuse caustic cleaning solutions. This

used to be done with UF membranes, but NF gives much better purification and BOD/COD levels and retains more colour which increases the possible level of reuse.

Ultrafiltration

UF is based on an even more open membrane than NF. A UF membrane will typically allow salts, organic acids, sugars and smaller peptides to pass through together with water, while large molecules like proteins, fat, carbohydrates, etc. will be rejected fully or partly, depending on the specific pore size of the membrane.

The osmotic pressure of such high molecular weight compounds is quite low, and therefore the process is performed at low pressure - usually in the range of 1-10 bar. The limiting factor in reaching high flux rates and well-defined separation is mainly related to the formation of gels on the membrane surface. Consequently, it is essential to operate with high velocities across the membrane surface in order to minimise this effect.

UF is a concentration and fractionation process somewhat similar to NF. In UF, however, the molecular level is different. An example is concentration of enzymes. Rennet is extracted from calf stomachs with a strong sodium chloride solution. Using UF, water, salt and certain unwanted organic compounds are removed, giving a product with increased purity and higher activity. The alternative process would involve some kind of evaporation in order to concentrate the product, and since enzymes are usually very sensitive to heat treatment, UF results in much reduced loss of enzyme activity.

Today UF is widely applied in the dairy industry. Treatment of whey in which the whey proteins are separated from lactose and salt and concentrated to high-value whey protein concentrate (WPC) is one of the most successful applications of UF membranes. Cheesemaking, milk protein standardisation, and production of milk protein concentrate (MPC) are just a few other examples of how membranes have influenced the dairy industry in the past 25 years.

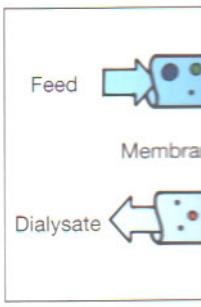
Microfiltration

MF utilises the most open type of membrane available. It is now possible to characterise the membrane by its pore size, which is typically in the range from 0.1 to 10 µm.

The trans-membrane pressure must be kept as low as possible (around 1 bar or less) in order to avoid secondary membrane formation. The key to controlling the process is to keep the trans-membrane pressure as low and as uniform as possible.

In the filtration spectrum (Figure 3), MF is placed between UF and conventional coarse filtration. For many years, MF has been used in a system where 'in depth' microfilters were mounted like traditional filters in correspondence with the traditional 'dead-end' filtration principle. The cross-flow filtration principle for MF has only been developed in recent years. The technique is similar to UF, meaning that the MF system can be used on a continuous basis without the need to take it apart for removal of the filter cake formed in traditional filters.

Among other things, microfilters are used to remove the remaining cloudiness in liquids in many different processes in the food, beverage, and pharmaceutical industries. In production of beer, filtration is used to remove all micro-organisms and colloidal particles in suspension in the beer, ensuring final product quality. The size of particles to be removed is normally between 0.1 and 10 µm.



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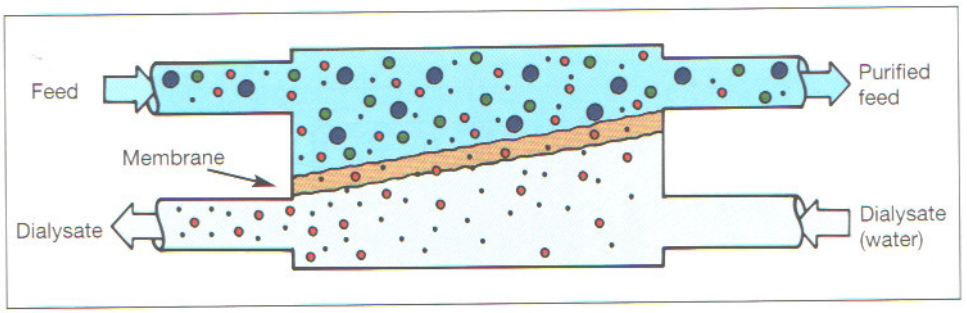

Figure 11: Dialysis. The feed stream is pumped counter-current on one side of the membrane to the dialysate stream. The concentration gradient is the driving force.

Microfilters are also used for removal of bacteria from air, for instance at the vents of sterile tanks.

This book concentrates on MF in its cross-flow form, i.e. the process is operated much like UF as described above, but with a more open membrane and at a lower trans-membrane pressure.

Applications for cross-flow MF vary from protein separation, and fat removal, to removal of bacteria and suspended solids.

MF of milk is playing an increasing role in the dairy industry, where it is used to improve the quality of milk for cheese-making and to extend the shelf life of market milk. In the brewing industry, tests are carried out to evaluate if cross-flow MF can replace conventional filtration using kieselguhr as a filter aid.

Dialysis

Conventional

In dialysis the concentration gradient is used as the driving force, and the process operates at normal atmospheric pressure. The feed is pumped through the system on one side of the membrane while dialysate (usually water) is pumped counter-current on the opposite side of the membrane.

Dialysis membranes are akin to the lower range of UF membranes and are usually prepared from cellulose polymers. They retain dissolved and suspended matter of molecular weight above 1,000, but permit the passage of ions and low molecular weight organic molecules like urea and alcohol which are removed in the dialysate stream. The principle of dialysis is shown in Figure 11.

The actual configuration of the dialysis membranes is usually in the plate-and-frame form or in the form of hollow fibres. The removal of toxins from the blood of patients suffering from kidney failures is probably the best established, safest, most effective, and most widely practised extra-corporeal life support procedure in use today. It is best known as haemodialysis.

Dialysis has found only limited industrial use. In the brewing industry it has been used to produce low-alcohol beer and it is known to give a very gentle de-alcoholisation with excellent conservation of the flavour compounds in ordinary beer. The alcohol in the dialysate can be recovered in a vacuum distillation column and the water can be reused in the process. (See Chapter 14).

Electrodialysis

Electrodialysis (ED) is defined as the transport of ions through non-selective semi-permeable membranes under the driving force of a direct current and an applied potential. The membranes used have both anion and cation exchange

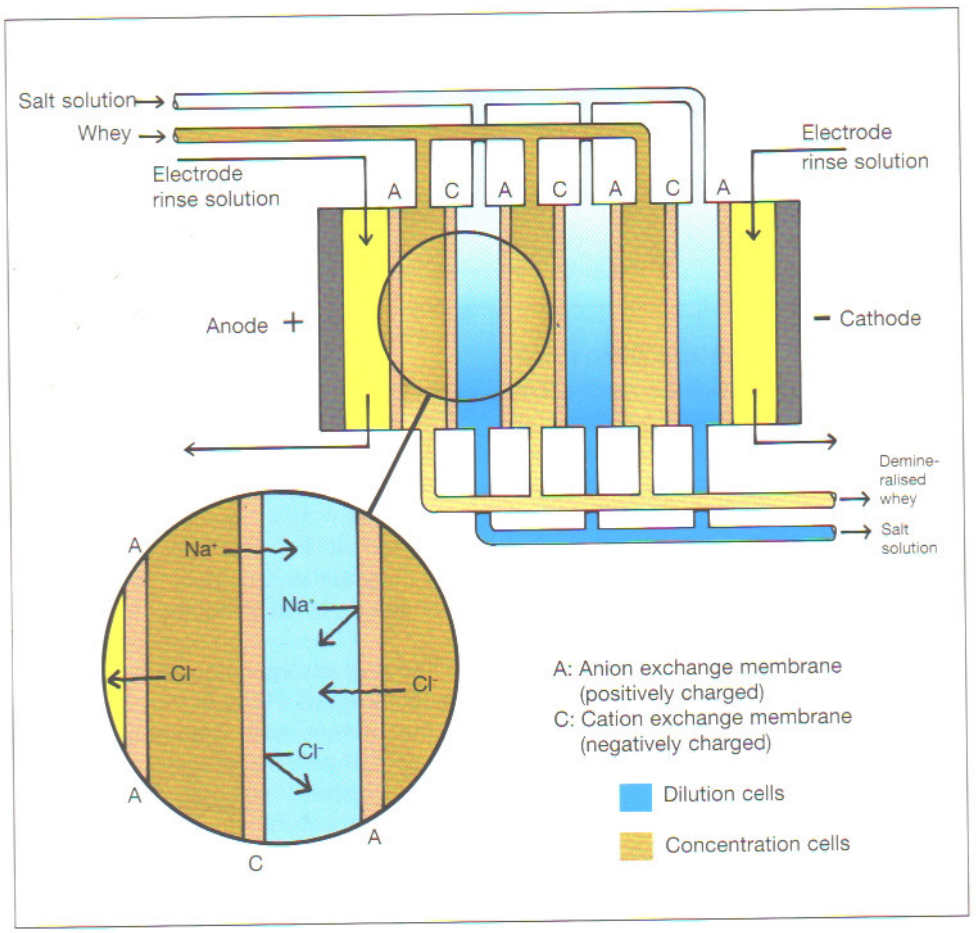

Figure 12: Electrodialysis. The feed solution is exposed to an electric field in a cell with alternating positively and negatively charged membranes. The charged molecules are removed from the feed stream by means of a salt solution.

functions, making the ED process capable of reducing the mineral content of liquids like sea and brackish water and whey.

In dialysis, the concentration gradient is the driving force in the process. In a way, ED is similar to dialysis, except that the driving force is now the electrical potential, and the membranes have a different structure.

ED membranes generally comprise polymers with charged functional groups covalently bonded to the polymer chain. Cation membranes are usually charged with sulfonate groups (SO_3^-), while anion membranes are charged with quaternary ammonium groups (NR_4^+). ED membranes are very robust, and it is common practice to open an ED stack, remove the membranes, clean them manually and remount them in the stack. This is only done if the normal daily CIP cleaning becomes insufficient. Figure 12 illustrates the operation of an ED cell.

In demineralisation of whey, the product is circulated through the dilution cells and a salt solution is circulated through the concentration cells. When the direct current is applied across the cells, cations will migrate to the cathode and anions to the anode. Completely free migration is, however, not possible because the membranes act as barriers to ions of like charge. The net result is depletion of ions in the whey. Consequently, the whey is demineralised to an extent determined by

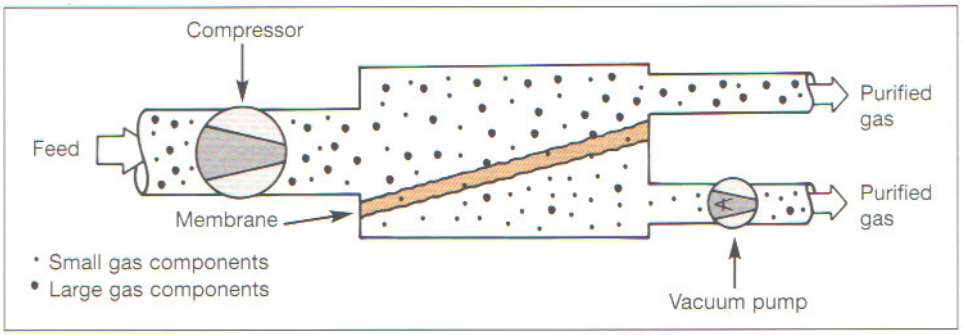

Figure 13: Gas separation. The mixture of gases is fed to the membrane system by a compressor, and the permeating gases are removed by a vacuum pump.

the ash content in the feed, residence time in the stack, current density, flow and viscosity.

The processing costs of ED very much depend on the demineralisation rate. Increasing the rate in steps from 50% to 75% to 90% doubles the processing costs per step. Demineralisation of whey should not be taken further than 50-70%, at which point the process is still economically feasible compared with ion exchange.

The rate of demineralisation can be improved if the whey is concentrated by NF prior to the ED process since this will remove some of the sodium chloride in the whey.

Gas separation processes

In gas separation the individual components in mixtures of gases can be separated. Pervaporation is a process in which dissolved gases in a liquid solution can be removed in a gaseous form.

Gas separation

Gas separation (GS) is a pressure-driven membrane process in which gas mixtures are separated by homogeneous porous membranes or by non-porous composite or asymmetric membranes. The actual separation mechanisms with the two types of membranes are very different. In GS using porous membranes, there is hardly any interaction between the gas molecules and the membrane material, and the gas concentration in the membrane is very low. The gas molecules must diffuse through a rigid membrane structure with the state of the polymer being hardly affected by their presence.

In porous membranes, the separation of two gases depends on the ratio of the square root of their corresponding molecular weights. This generally means that the separation that can be achieved with porous membranes is relatively low, and in order to obtain a high level of separation, it is necessary to use a cascade operation. This is rather unattractive from a financial point of view, and the only industrial application so far has been in the nuclear industry for uranium hexafluoride isotope separation.

GS through non-porous membranes depends on differences between the permeabilities of various gases through a given membrane.

GS membranes are manufactured from elastomers and glassy polymers. In general, permeability through a rubbery material (elastomer) is much higher than through glassy polymers because of a higher mobility of the polymer chain segments. In contrast, the selectivity of glassy polymers is higher.

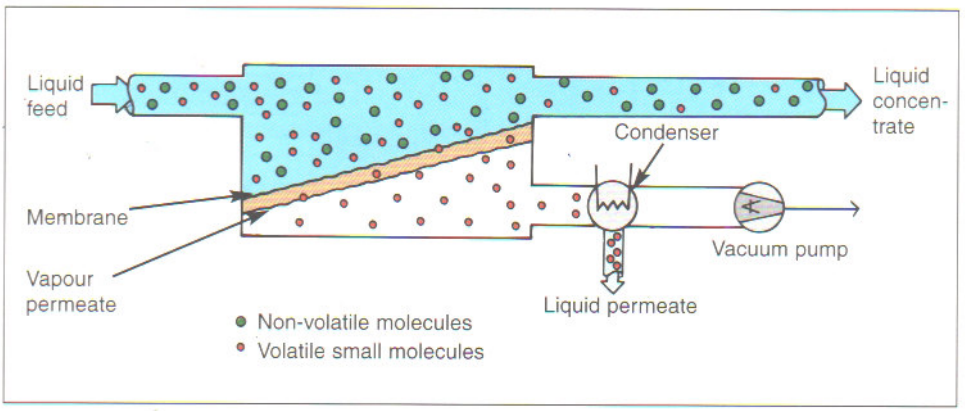

Figure 14: Pervaporation. A liquid mixture is fed into a membrane system where a vapour can permeate the membrane. This is caused by partial vaporisation of volatile components from the feed stream.

In practice, the membranes need to combine a high flux with a reasonably high selectivity. Typical membrane materials are silicone rubber, natural rubber, polystyrene, polyamide, polycarbonate, polysulphone and cellulose acetate.

Figure 13 is a schematic drawing of a GS process where the feed is pressurised by a compressor, and the permeate removed through a vacuum pump. The pressure applied on the upstream side may be in the order of 100 bar.

Amongst the many different applications of GS are purification of methane (CH_4) from landfill drainage gas, purification of methane from natural gas, and recovery of carbon dioxide in enhanced oil recovery. GS can also be effected to obtain oxygen enriched air or nitrogen enriched air. Oxygen enriched air is used to enhance combustion and for various medical and biotechnological applications, while nitrogen enriched air can be used as an inert gas in the blanketing of flammable liquids in fuel tanks, and as a sealant gas to prevent oxidation of foods.

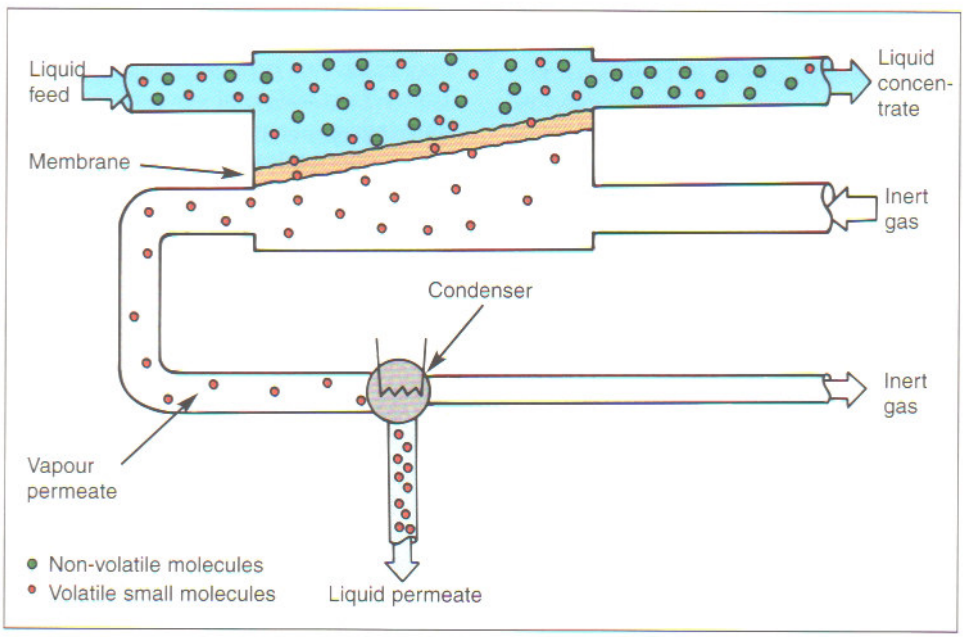

Figure 15: Pervaporation. The liquid may also be removed by sweeping an inert gas through the permeate system, and condensing the vapour.

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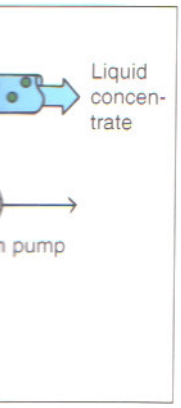

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Recovery of volatile organic compounds and drying of compressed air will be discussed at the end of Chapter 14.

Pervaporation

The discovery of pervaporation (PV) goes back to 1917. In 1982, the first industrial plant was installed in Brazil for production of anhydrous ethanol, but the process has not yet had a real industrial breakthrough.

PV is a separation technique in which a liquid feed is separated by partial vaporisation through a non-porous membrane with selective properties. This results in a vapour permeate and a liquid concentrate. The driving force for the mass transfer of gasses from the feed to the permeate is a gradient in chemical potential, which is established by the application of a difference in the partial pressures of the gasses across the membrane. This difference in partial pressure can be created either by reducing the total pressure on the permeate side of the membrane, using a condenser and vacuum pump system as illustrated in Figure 14, or by sweeping an inert gas on the permeate side of the membrane as illustrated in Figure 15. The two different processes are known as vacuum PV and sweep gas PV. Vacuum PV is the most common mode of operation. In both processes the vapour permeate is transformed into a liquid by means of a condenser.

The membranes for PV are non-porous, usually with an asymmetric morphology with a dense top layer and an open porous sub-layer, as found in asymmetric membranes for RO and UF. The membranes may also be of the thin film composite type. The polymers used are typically polyacrylonitrile (PAN) or polyvinyl alcohol (PVA), which give high selectivity.

Most applications are in the chemical industry, but there are also some in the food and pharmaceutical industries. Even traces of water can be removed from alcohol or other organic solvents. PV is also able to break azeotropic mixtures like ethanol with 4.4% water, which cannot be achieved by ordinary distillation. PV may also be used for production of low-alcohol beer from ordinary beer through removal of the alcohol in the permeate. In the environmental sector, it is possible to remove volatile organic contaminants from waste water or in analytical applications to enrich a given component for quantitative detection.

Resin-based processes

Resins are beads or granules of organic, or sometimes inorganic materials, which have the ability to absorb molecules under certain conditions. The retained molecules can be selectively released by various means, and this makes it possible to separate various types of components.

In ion exchange, the resins retain molecules in the form of ions, while chromatography retains molecules based on a range of different properties like charge, size, shape, affinity, etc.

Ion exchange

In the section on ED above, it was shown how ions could be removed from a solution by means of a cell composed of anion and cation membranes, placed alternately between an anode and a cathode, using electrical current as the driving force.

Ion exchange (IE) employs resin beads to adsorb minerals from a solution in exchange for other ionic species. The resins have a defined maximum capacity for how much material they can adsorb. When they are completely saturated, the adsorbed minerals must be removed and the resins regenerated before reuse. The resins are normally packed in fixed

columns of suitable design, but it is also possible to process the resins in a stirred tank.

Ion exchange resins are macro-molecular porous plastic materials, formed into beads with diameters in the range of 0.3 to 1.2 mm for technical applications. Chemically, the resins are similar to electrodialysis membranes with a base structure consisting of polystyrene cross-linked with divinyl benzene in which both anion and cation exchange groups have been introduced. The anion exchange groups are of the quaternary ammonium type (NR_4^+), while the cation exchange groups are of the sulfonate type (SO_3^-).

The resins are able to exchange the mobile ions they contain for ions of the same charge contained in the solution to be treated. This is shown here in a simplified form for sodium chloride removal, where R stands for the exchange group bound to the insoluble resin:

Cation exchange

$$R - H + Na^+ \rightleftharpoons R - Na + H^+$$

resin in H^+ form

Anion exchange

$$R - OH + Cl^- \rightleftharpoons R - Cl^+ OH^-$$

resin in OH^- form

The reaction is written as an equilibrium because the direction of the reaction depends on the ion concentration in the liquid, and in the solid phase of the resin.

The equilibrium constant is variable and depends on the ionic species, which makes the ion exchange process selective. Generally speaking, multivalent ions have higher selectivity than monovalent ones, and ions of the same valence are selected by size, large ions having higher selectivity. For cations the selectivity decreases in the order of:

$Ca^{2+} > Mg^{2+} > K^+ > Na^+$.

In the same way the selectivity of anions can be classified as follows:

$citrate^{3-} > HPO_4^{2-} > NO_3^- > Cl^-$.

IE is used where high levels of demineralisation are required. Treatment of tap

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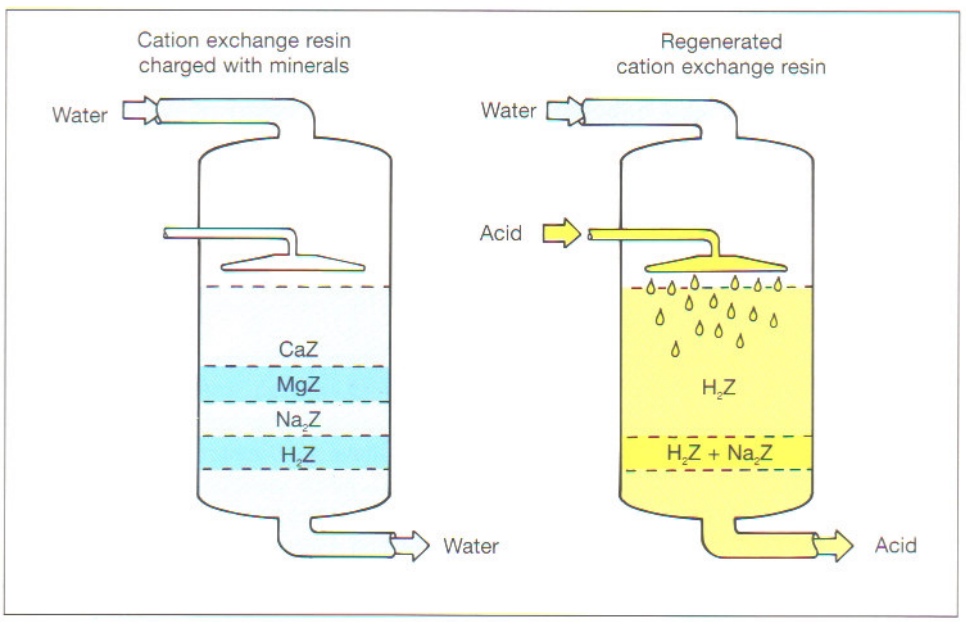

Figure 16: Ion exchange. In a cation exchange column the positively charged cations are captured by the resin. When the resin has saturated, the resin bed is flushed with water, and the cations are removed through the regeneration process by means of an acid.

water for use in high-pressure boilers is a typical ion exchange operation, in which all minerals are removed by passage through several ion exchange columns. IE has also been used for whey demineralisation in cases where a demineralisation rate of 90% is required.

Even though IE is an excellent tool for demineralisation, it has some drawbacks such as high consumption of water and regeneration chemicals. The resins may also be sensitive to plugging of suspended solids or substances which may precipitate during the demineralisation process.

Figure 16 shows how a cation exchange column is charged with minerals and subsequently regenerated with acid, and brought to the hydrogen ion form ready for the next cycle.

Chromatography

In its simplest form, a chromatographic separation system consists of a column filled with separation resin beads. Figure 17 illustrates the principles of operation.

In step 1, a liquid mixture consisting of two components (green and red droplets) is added to the top of the column. In step 2, an eluent (blue droplets), normally de-ionised water, is added to help move the material through the system. As the liquid begins to flow through the resin, the green component is temporarily attracted, and slowed down, while the red component passes down through the column more easily, gradually becoming separated from the green component. In step 3, the separation of the two components becomes distinct and the relatively pure, red component is drawn off at the bottom of the column. In step 4, the green component finally reaches the outlet as a relatively pure solution.

Liquid chromatography (LC) techniques are widely used for the separation, isolation, purification and analytical characterisation of both high and low molecular weight compounds in the laboratory, as well as on the industrial scale in various sectors in the food and pharmaceutical industries.

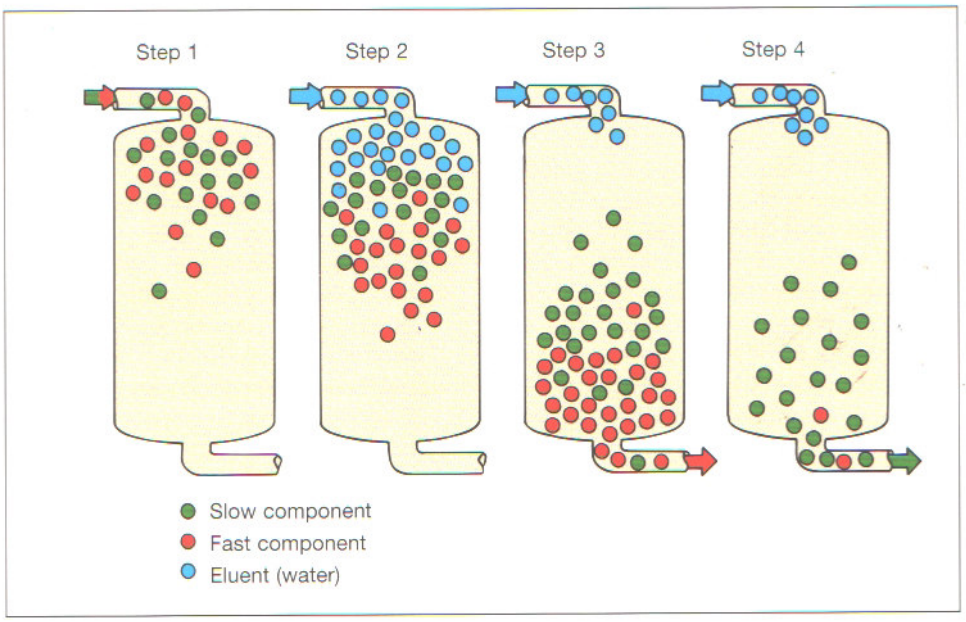

Figure 17: Chromatography.

LC techniques are usually classified into five categories:

- *Distribution* which utilises the differential solubility of a substance in two immiscible liquid phases
- *Adsorption techniques* based on non-specific adsorption of the target molecules on solid-phase supports such as aluminia or silica gel
- *Ion exchange chromatography* which separates molecules by electrostatic interactions
- *Gel permeation techniques* based on molecular sieve effects of the adsorbent particles that separate molecules based on their size and molecular weight
- *Affinity chromatography techniques* based on biospecific sorption, group-specific interaction or chemisorption of the target molecules on appropriate solid phases

LC has been known since the turn of the century, but its primary use has been in the analytical sector, where the excellent separation capability has been indispensable. The industrial use of this technology on a production scale has, however, been fairly limited and mainly for high value-added products in the pharmaceutical industry. Low processing rates and difficulties in scaling-up chromatographic separation from laboratory to production levels have hampered its broader use and acceptance.

Traditionally, chromatography has been performed by flowing a sample down long, narrow axial columns filled with soft gel-like resins. Such column geometry allows operation at high linear velocities, but produces high back pressure and compression of the resin matrix. This initiates a rapid rise in pressure and a reduced flow of sample. The increase in pressure drop contributes to reducing the life time of the resin material. Furthermore, there may be a risk of formation of channels along the axis of the column, which will lead to poor utilisation of the resin material in the column. This has made industrial scale operation of chromatography troublesome and expensive. Efforts to overcome these problems have led to the development of more robust resins and a new chromatography column based on the Radial Flow Chromatography (RFC) principle, which will be discussed in Chapter 10.

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4 Membranes

A membrane is defined as an intervening structure, separating two phases and/or acting as an active or passive barrier to the transport of matter between the phases adjacent to it. This is a very general definition and this chapter will examine more closely what a membrane actually is, in terms of how it functions, how it is composed both physically and chemically, how its properties are characterised, and how it is manufactured.

A membrane can be thick or thin; its structure can be homogeneous or heterogeneous; transport can be active or passive, passive transport can be driven by pressure, concentration or a temperature difference; membranes can be natural or synthetic, synthetic membranes can be organic or inorganic; and membranes can be neutral or charged.

In order to get this very wide concept of membranes into a more systematic scheme, membranes can be classified from different viewpoints. The first distinction is between synthetic and natural membranes. Natural membranes are biological in nature, and can be subdivided into living and non-living membranes.

Living membranes are an essential part of all living organisms, since they perform vital functions in regulating the exchange of salts, nutrients and metabolic products between cells and their environment. Non-living natural membranes can be phospholipids and lipoproteins surrounding triglycerides in milk fat, forming the fat globules in milk.

This book will deal only with synthetic membranes.

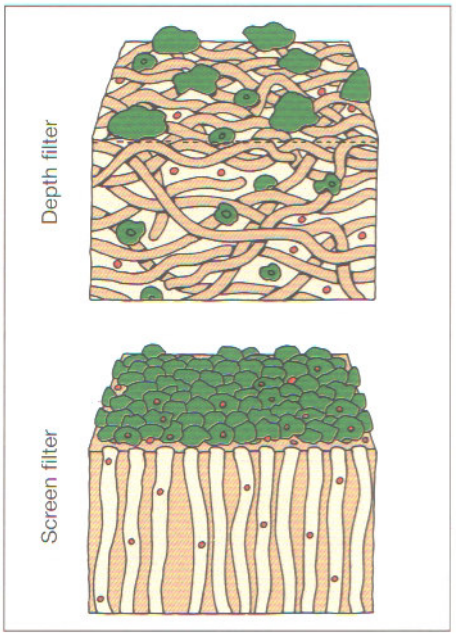

Figure 18: Depth filters versus screen filters. In a depth filter the randomly oriented fibres are trapping particles, while a screen filter retains particles larger than the pore size of the filter.

Depth versus screen filters

Membrane filtration is frequently compared with conventional filtration just as the membrane itself can be compared with a conventional depth filter.

Depth filters get their name from the fact that filtration or particle removal occurs within the depths of the filter material. Depth filters consist of a matrix of randomly oriented fibres or beads bonded together to form a tortuous maze of flow channels as illustrated in Figure 18. Particles which are insoluble or colloidal in nature are removed from a fluid by entrapment or adsorption to the filter matrix.

A screen filter separates by retaining particles on its surface in much the same manner as a sieve. The structure is usual-

ly more rigid, uniform and continuous, with the pore size controlled more accurately during manufacture. Membrane filters fall into this category. Unlike depth filters, there is almost no danger of material migration, and 'grow through' of micro-organisms is usually not a problem, provided the membranes are cleaned and disinfected according to instructions. Since screen filters have a defined pore size, they can be given an absolute, or quantitative rating.

Micro-porous versus asymmetric membranes

Membranes are also classified by morphology or structure. Figure 19 shows how synthetic membranes may be characterised as symmetric or asymmetric membranes.

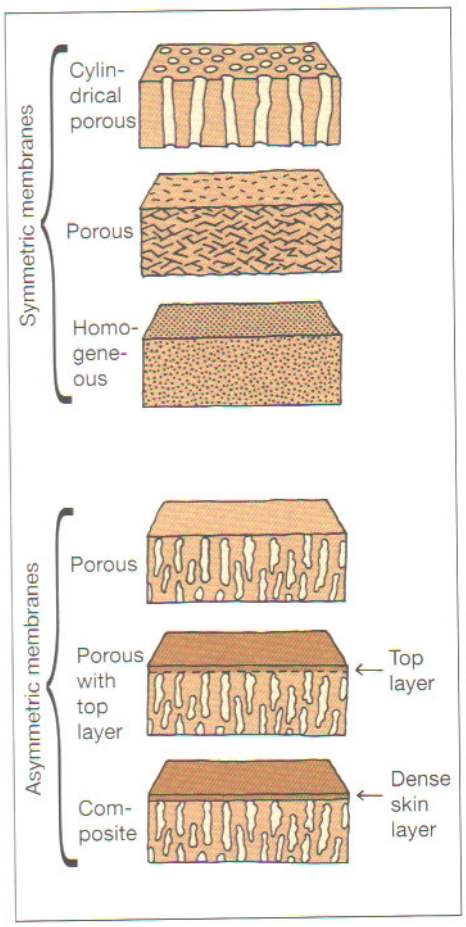

Figure 19: The structure of symmetric and asymmetric membranes.

The micro-porous (symmetric) membranes are characterised as cylindrical porous, porous or homogeneous.

The thickness of symmetric membranes ranges roughly from 10 to 200 µm and the resistance to mass transfer is determined by the total membrane thickness. A decrease in membrane thickness results in an increased permeation rate.

A breakthrough in industrial applications of membranes was the development of asymmetric membranes. They consist of a very dense top layer or skin with a thickness of 0.1-0.5 µm supported by a porous sub-layer with a thickness of about 50-200 µm. Such membranes combine the high selectivity of a dense membrane with the high permeation rate of a very thin membrane.

The porous substructure may have a finger-like structure, or the more uniform sponge structure. Asymmetric membranes are divided into porous, porous with top layer, and porous with dense skin layer, also called thin film composite (TFC) membranes.

TFC membranes are in fact skinned asymmetric membranes, where the top layer and sub-layer originate from different polymer materials, in order to optimise the benefits of each layer independently.

Micro-porous membranes are sometimes further classified as 'isotropic' (with pores of uniform size throughout the thickness of the membrane) or 'anisotropic' (with pores changing in size from one surface of the membrane to the other). The terms 'anisotropy' and 'asymmetry' are frequently used interchangeably. Micro-porous membranes are designed to retain all particles above

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its rating. A 0.45 µm membrane implies that its largest pore is 0.45 µm or less, which means that all particles above 0.45 µm will be retained. However, particles that are approximately the same size as the pores may penetrate partially into the pores and block them.

Asymmetric membranes, on the other hand, are characterised by the thin skin on the surface, which determines the rejection properties. Such membranes will retain molecules above a certain molecular weight (cut-off value). They do not have the same tendency to block as micro-porous membranes, although, like all filters, they are susceptible to flux decreases from fouling and concentration polarisation. The differences between micro-porous and asymmetric membranes are illustrated in Figure 20.

All the types of membranes referred to here are based on solid polymers or, in some cases, ceramics or glass. However, separation can also occur through a liquid film in which a component is soluble and thereby transported by diffusion. Such films are characterised as 'liquid membranes'.

Membrane materials and membrane chemistry

Most membranes are made from organic polymers and are consequently similar to plastic films, except that most membranes are produced in a wet form. Originally, membranes were kept wet during storage, but today membranes are commonly dried through a special procedure which leaves the membrane structure undamaged. There are hundreds of polymers which can form plastic films, but there are only few which are good candidates for membrane manufacture. Some of the more basic requirements of polymers for making membranes are the following:

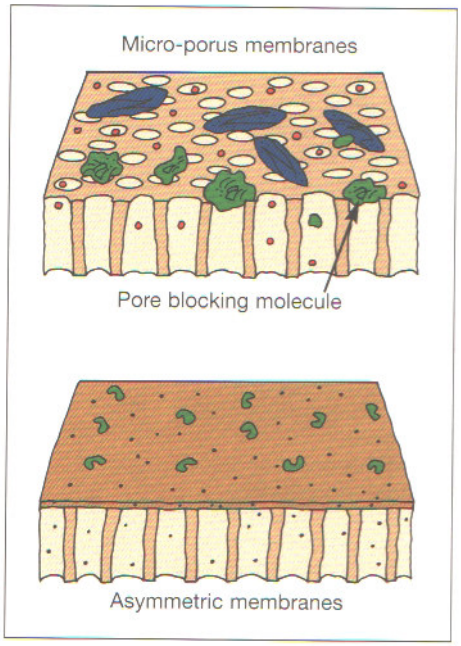


Figure 20: Micro-porous versus asymmetric membranes. The pores of micro-porous membranes may become blocked by particles of certain shapes, and a size close to that of the pores. With an asymmetric 'skinned membrane', particles do not enter the skin, and cannot cause the same blocking effect by entering the body of the filter.

- The polymer must form a good film
- The polymer must possess hydrophilic groups which can hydrogen bond to water to enable it to enter the membrane structure
- The polymer must have high swelling characteristics
- The polymer must have a high wet strength
- The polymer must be able to exist in thin layers in order to reduce the resistance to permeate flow
- The polymer must have good properties with respect to pH and temperature variations

In porous membranes for MF, it is the pore size and the pore size distribution which determine the throughput and selectivity of the membranes, and this may reduce the importance of some of the above criteria. Table 5 gives a list of polymers used for commercially available membranes for MF, UF and RO.

Cellulose acetate

As previously mentioned, the break-

Table 5: List of polymers used for production of commercial membranes.

Polymer	Abbreviation	Application		
		MF	UF	RO
Cellulose acetate	CA	X	X	X
Cellulose triacetate	CTA	X	X	X
Cellulose acetate/-triacetate blend	CA/CTA			X
Cellulose nitrate	CN	X		
Cellulose/regenerated	RC	X	X	
Gelatine	GE		X	
Polyacrylonitrile	PAN		X	
Polyvinylchloride	PVC	X		
Polyamide/aromatic	PAN	X	X	X
Polysulphone	PS	X	X	
Polybenzimidazole	PBI			X
Polybenzimidazolone	PBIL			X
Polycarbonate/track-etched	PC	X		
Polyimide	PI		X	X
Polypropylene	PP	X		
Polytetrafluorethylene	PTFE	X		
Polyvinylidenefluoride	PVDF	X	X	
Polyacrylic acid + zirconium oxide/skin			X	X
Polyethyleneimin + toluene diisocyanate skin of TFC membrane				X

through in membrane filtration was the *Loeb-Sourirajan* cellulose acetate (CA) membrane.

The raw material for CA is cellulose, which is a polymer of β-1,4 linked glucose units. On each glucose unit there are three free hydroxyl groups which will react with acetic acid and form acetyl groups (CH_3COO-groups) by eliminating water. If all three hydroxyl groups are replaced, cellulose triacetate (CTA) is formed which contains 44.8% acetyl groups. CTA is however insoluble in acetone, which causes problems in manufacturing. By carefully controlling the hydrolysis of CTA, the acetyl content may be reduced to 38-40% corresponding to a CA with an average of 2.5 out of 3 hydroxyl groups having been replaced by acetyl groups.

Cotton is usually the source for the purest form of cellulose, the highest in molecular weight, and the narrowest in molecular weight distribution which are all properties favourable for the production of strong and flexible membranes.

CA membranes, however, have severe limitations. Being an ester and a polysaccharide it is subject to hydrolysis which confines its use to a pH range of 3-7 and an upper temperature limit of 35°C. This imposes restrictions on the way the membranes can be cleaned. Membranes produced on the basis of a mixture of CA and CTA (dioxane is used as solvent for CTA) have better temperature and pH resistance, and these membranes are still used today due to their excellent performance in terms of flux rates and salt rejection.

Eastman Kodak (USA) was one of the pioneers in the production of CA membranes because CA is also used in the manufacture of photographic films. Figure 21 illustrates the chemical formula for CA.

Polyamide

Polyamide (PA) is characterised by having an amide bond in its structure (-CO-NH-). Aliphatic PA represents a very large class of polymers (Figure 22), but aromatic PA (Figure 23) is preferred as

membrane material because of its outstanding mechanical, thermal, chemical and hydrolytic stability, as well as excellent salt rejection in RO. PA is resistant in the pH range of 3-11 and can withstand temperatures of up to 35°C. However, PA is easily attacked by free chlorine with a tolerance limit much lower than CA. Figure 24 illustrates the free chlorine tolerance levels for CA, CTA and PA.

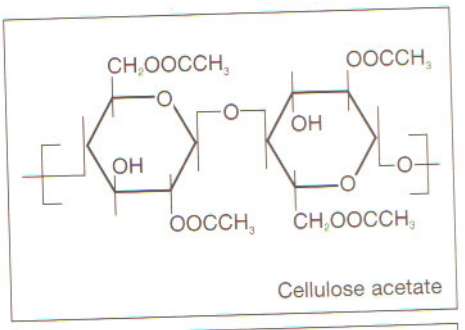
PA is used for RO, UF and MF membranes, but is known especially for RO membranes through the early work of DuPont, Delaware, USA, who used it for production of the hollow fine fibres system, consisting of hollow fibres with an inside diameter of 42 µm. A bundle of millions of hollow fibres were placed in one element giving a very high membrane surface area in a small volume.

Despite its low tolerance to chlorine, PA in the shape of hollow fine fibres has been one of the most common systems used for desalination of sea and brackish water. More recently, PA has been used in connection with the production of thin film composite membranes to form the thin barrier layer.

Polysulphone

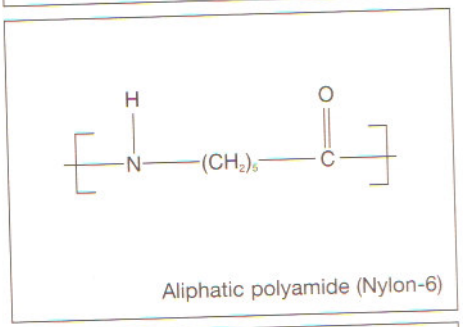
Polysulphone (PS) is widely used as the basic polymer for UF membranes. The structure of PS is shown in Figure 25. It is characterised by the diphenylene sulphone repeating units and the -SO_2- group which both contribute to the stability of this unique polymer.

PS was a breakthrough in UF, and especially for the application of UF in industries where cleaning and hygiene are of the utmost importance. Today, PS is the most common membrane material for milk, whey, enzyme and protein treatment. It is also commonly used as the support membrane for thin film composite RO and NF membranes.



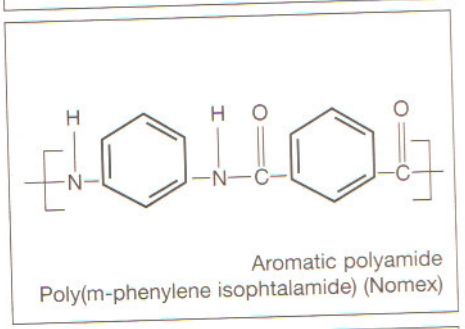
Cellulose acetate

Figure 21: Cellulose acetate (CA).



Aliphatic polyamide (Nylon-6)

Figure 22: Aliphatic polyamide (PA).



Aromatic polyamide
Poly(m-phenylene isophtalamide) (Nomex)

Figure 23: Aromatic polyamide (PA).

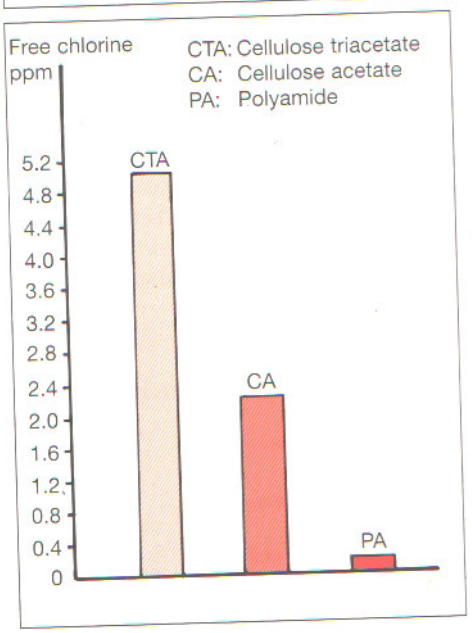


Figure 24: Chlorine tolerance levels for membranes. Polyamide membranes are generally very sensitive to chlorine, whereas cellulose acetate membranes have a relatively good resistance to chlorine. Cellulose triacetate exhibits exceptionally good chlorine resistance.

Figure 25: Polysulphone (PS).

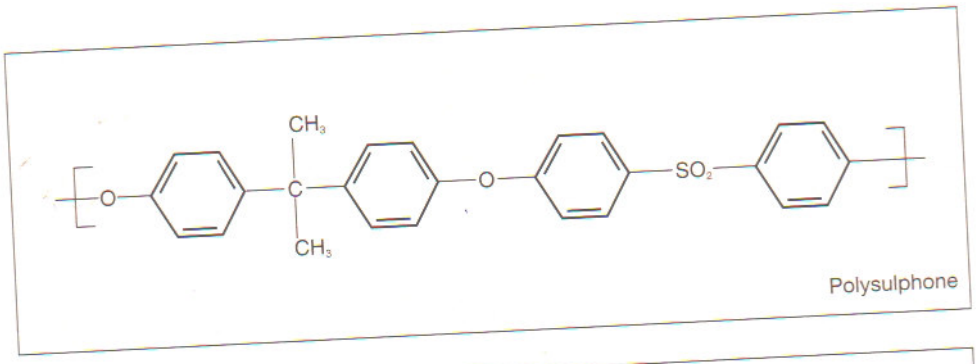
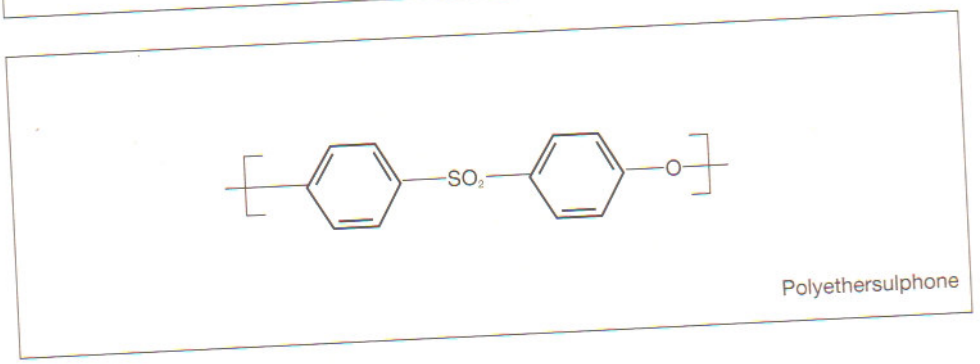


Figure 26: Polyethersulphone (PES).



PS membranes tolerate pH in the range of 2-13 and temperatures as high as 80°C, and they are much more tolerant to chlorine than most other organic polymers. PS membranes can even be sterilised at 121°C, which is an advantage for applications in the biotechnology sector. Some manufacturers permit chlorine up to a level of 200 ppm for short term sanitation purposes, and 50 ppm for long term storage at temperatures below 35°C.

The membrane is fairly easy to manufacture and it is possible to make membranes with cut-off values in the range from 1,000 to 500,000 MW.

Polyethersulphone (PES) (Figure 26) presents even better properties with respect to resistance to pressure, and several manufacturers are using PES for the production of UF membranes.

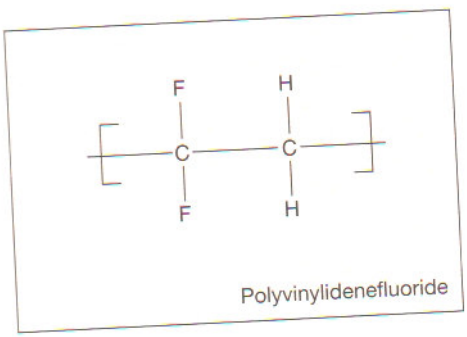
Polyvinylidenefluoride

Polyvinylidenefluoride (PVDF) (Figure 27) is a fluor polymer used for manufacture of UF and MF membranes. PVDF is highly chemical resistant, it has a good temperature resistance and can be autoclaved repeatedly.

The membranes tolerate pH in the range of 1-11, temperatures of up to 60°C, and they are even more tolerant to chlorine than PS membranes. Some manufacturers permit the use of 1,000 ppm chlorine at temperatures below 35°C.

PVDF is also more resistant to organic solvents than PS, and it is widely used for the treatment of oil emulsions and electrophoretic paint. The range of cut-off values is similar to that of PS membranes.

Figure 27: Polyvinylidenefluoride (PVDF).



Polytetrafluorethylene

Polytetrafluorethylene (PTFE) or teflon (Figure 28) is used for certain types of MF membranes. It is a highly chemical resistant polymer and can be exposed to temperatures as high as 200°C. Normally it will be the membrane system which sets the limit for the maximum operating temperature.

PTFE is not soluble in any organic solvent. This gives the membrane properties beyond any other membrane material, but it also means that the membranes cannot be produced in the conventional way by dissolving the polymer in organic solvents and casting it into a suitable configuration. PTFE membranes are therefore prepared by sintering and stretching the polymer in order to form a suitable, porous structure.

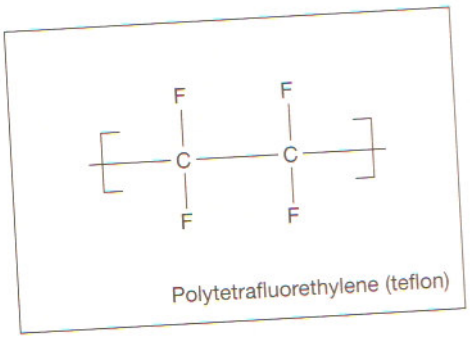


Figure 28: Polytetrafluorethylene (PTFE).

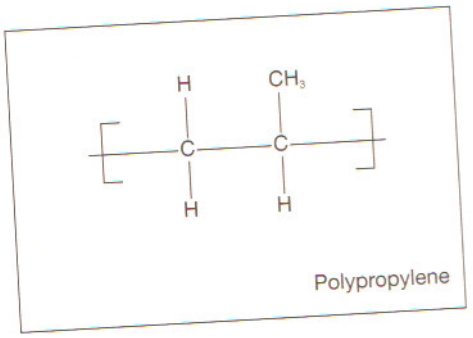


Figure 29: Polypropylene (PP).

Polypropylene

Like the two previously mentioned fluor polymers, polypropylene (PP) (Figure 29) is also an excellent solvent resistant polymer. They are all hydrophobic in nature, which means that water cannot wet such membranes spontaneously. When used in conjunction with aqueous mixtures, they have to be pre-wetted by appropriate wetting agents like alcohol. PP membranes are mostly known as fibres and are used as MF and gas separation membranes.

Thin film composite membranes

Thin film composite membranes (TFC) membranes have a thin, dense polymer skin or barrier layer formed on top of a porous support structure. In this way, their structure is similar to the asymmetric membranes, except that the barrier layer and support structure are formed in two different steps - usually from two different polymers.

There are different methods for the manufacture of TFC membranes. These are reviewed in the section on membrane manufacture at the end of this chapter.

One of the better known TFC membranes is the Film-Tec FT-30. It is based on a UF PS micro-porous membrane as support. The PS is usually supported by a non-woven polyester paper or a non-woven PP paper. The barrier layer is formed by dip-coating the support film in a water solution of an amine, followed by immersion in a bath with an acid chloride dissolved in an organic solvent. The two highly reactive monomers (amine and acid chloride) will combine to form a very thin, dense barrier layer of PA. The reaction may be accelerated by applying heat to complete the interfacial reaction. The selection of amine and acid chloride is decisive for the properties of the membrane. Usually, monomers containing aromatic structures are selected since they provide the best physical and chemical properties combined with excellent selectivity and permeability properties.

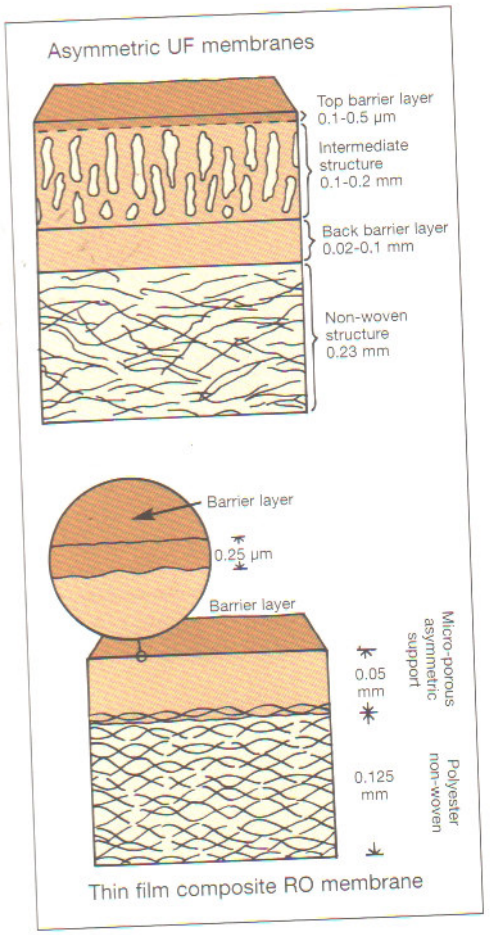


Figure 30: Membrane support material. Membranes are usually cast onto a support material in the form of a sheet of non-woven polymer fibres. The figure shows a UF membrane cast onto a polypropylene non-woven material and an RO thin film composite membrane with a non-woven polyester support.

The structure of the TFC membrane is illustrated in figure 30. The combination of the non-woven support covered with a UF type PS membrane with a specially tailored pore structure, and the final coating with a very thin barrier layer of a very resistant aromatic PA, represents an important milestone in the development of improved membranes for industrial use.

Dialysis membranes

Cellophane and cuprophane are probably the most common polymers for dialysis membranes. They are both based on regenerated cellulose. Other materials are cellulose acetate and polyvinyl alcohol. The membranes are homogeneous nd between 10 and 100 µm in thickness.

Electrodialysis membranes

As described in Chapter 3, ED membranes are manufactured from cation and anion exchange resins based on polystyrene cross-linked with divinyl benzene. The membranes are non-porous and usually homogeneous in structure with a thickness of 100-500 µm.

The membranes are produced in sheet form, supported by synthetic fibres and have a high mechanical and chemical stability. If necessary, they can be removed from the ED stack and cleaned mechanically before remounting.

Gas separation membranes

Membranes for gas separation are either of the thin film composite type or asymmetric membranes, based on elastomeric polymers like polydimethylsiloxane, polymethylpentene, or glassy polymers like polyimide or polysulphone.

Membranes for pervaporation fall into two categories:

- Membranes based on *hydrophilic* polymers such as polyvinylalcohol or cellulose acetate, which preferentially permit the permeation of water, are used for removal of water from mixtures of water and organic solvents.

- Membranes based on *hydrophobic* polymers such as polydimethylsiloxane, which preferentially permit permeation of organic substances, may be used for aroma recovery and removal of traces of organic components from water.

Ceramic membranes

Ceramic membranes are also called inorganic membranes or mineral membranes to distinguish them from organic membranes. Ceramic membranes are mostly used for MF applications, but it is also possible to make UF and even NF ceramic membranes.

Some of these are in reality 'dynamic' membranes formed by deposition of inorganic solutes onto micro-porous supports. The first mineral membranes were produced by SFEC (Societé de Fabrication d'Elements Catalytiques) under a licence agreement with Union Carbide and were based on porous carbon tubes coated with zirconium oxide.

Today, ceramics are formed by the combination of metals such as aluminium, titanium or zirconium with a non-metal in the form of an oxide, nitride or carbide. Ceramic membranes prepared from these materials are typically aluminia oxide supports, coated with different types of aluminia oxides, titanium oxide, zirconium oxide, or combinations. Such membranes have excellent properties with respect to temperature resistance, they cover the full range, and they are not attacked by organic solvents. They are usually made as multi-channel elements in which the individual channels have a diameter of 2.5 to 10 mm. A more recent development is a honeycomb structured element based on a similar technology as the catalytic converters in automobile exhaust pipes.

Compared with conventional organic membranes, ceramic membranes are very expensive. This is to some extent compensated by a longer lifetime, since, in theory, ceramic membranes will never wear out.

Membrane support material

The physical strength of membranes is essential to their successful application in industry. Whether membranes are cast into flat sheets, tubes or other configurations, they are usually not sufficiently strong to support themselves. Originally, they were supported by filter paper, but membranes of today are normally cast directly onto a non-woven support based on polyester or polypropylene.

The strength and chemical stability of the support material are essential for the lifetime of the membrane. Also the thickness of the support and consequently the thickness of the total membrane is important since it provides strength, but it can also be decisive for the dimension of the final flow channel and determine how much membrane area can be fitted into a spiral-wound element.

Some membrane configurations are based on self-supporting structures like the hollow fine fibre and hollow fibre modules. In such cases, the thickness of the fibre wall provides the strength necessary for the operating pressure the element is designed for. Since the resistance to flow through the membrane increases with increasing wall thickness, the optimisation of pore/tube diameter becomes important for the total performance of such membrane elements.

Figure 30 illustrates how flat sheet UF and thin film composite membranes are composed in order to give sufficient strength to withstand the high pressures membranes are exposed to. The bonding between the various layers is essential to prevent membrane rupture in instances where the system is exposed to back pressure.

Membrane properties and characteristics

Membranes are involved in a wide range of separation problems, and a specific membrane structure is required to solve each task in the optimal way. The characterisation of membranes is essential in order to predict the performance of a specific membrane for a specific separation task. The need for membrane characterisation can be summarised as follows:

- Method to predict performance on specific products

- Method to compare different types of membranes
- Method to secure restoration of performance after membrane cleaning
- Method to predict membrane lifetime
- Quality control parameter
- Key to determine reproducibility of membrane production

There are basically two approaches to membrane characterisation:

- *Theoretical.* This includes a large number of different techniques like thermoporometry, permporometry, scanning electron microscopy, and various permeability methods

- *Practical.* This includes measurement of water fluxes, rejection/permeability values for specific solutes such as sodium chloride, saccharose, dextranes and polyvinylpyrrolidone, bubble point, molecular cut-off values, temperature range, pressure range, pH range, resistance to organic solvents, and resistance to detergents and cleaning agents

For the more theoretical part, readers are referred to other literature on this subject. The following sections will deal with the more practical approach used by manufacturers of membranes and membrane systems.

This chapter will deal mainly with the properties of the membranes. The remaining part of a membrane system also involves polymers, which may be influenced by the above-listed parameters, but in most cases the membrane itself turns out to be the weakest link.

Water flux

Water flux is measured on pure water or weak salt solutions at standardised temperatures and pressures. The flux is measured in litres/m^2/hour (lmh) at 20-25°C.

UF membranes typically have pure water fluxes of 100-1,000 lmh measured at 5 bar, while RO/NF membranes have fluxes in the range of 10-100 lmh measured with a 0.25% NaCl solution at pressures of 30-40 bar.

MF membranes have water fluxes in the range of 100-1,000 lmh measured at 1 bar. However, the water flux for MF membranes is only of limited value, and a better characterisation is achieved through bubble point and pore size measurements.

Permeability

Salt permeability or salt rejection is an important parameter for RO and NF membranes. Salt rejection was previously defined as:

$$R = (1 - c_p/c_f) \times 100$$

and permeability as:

$$P = c_p / c_f \times 100 \text{ and } R + P = 100$$

Permeability is a characteristic property of the membrane which illustrates its ability to retain specific chemical compounds such as salt and sugar. Permeability depends on the size, shape and charge of molecules and ions in the feed. For a given membrane, the permeability of di-valent salts is smaller than that of mono-valent salts, while di-saccharides like saccharose has an even lower permeability due to its larger size.

In a membrane system, the feed concentration of a given solute which is rejected will increase throughout a continuous plant with a large number of modules in series. In those cases, the apparent permeability is defined as:

$$P_{app} = (1 - (1 - \alpha)^P) / \alpha$$

where P is the membrane permeability, α is the water recovery, which is the fraction of the feed converted to permeate.

If the water recovery for desalination of brackish water with 6,000 ppm salt is 65%, and the membrane permeability is 5%, then the apparent permeability is calculated to be 7.9%, giving a salt concentration in the average permeate of 474 ppm.

Permeability changes with pressure, temperature and concentration. Normally, increasing pressure will increase the rejection, but it depends on the conditions, and it greatly depends on surface layer phenomena such as concentration polarisation and membrane fouling as described in Chapter 6.

Bubble-point method

The bubble-point method is a very simple technique for characterising the large pores in MF membranes. The method essentially measures the pressure needed to blow air through a liquid-filled membrane. The membrane is placed in a filter device where the top of the filter is filled with a liquid (normally water or alcohol) which fills all the pores of the membrane. The bottom of the filter is in contact with air, and the air pressure is gradually increased.
At a certain pressure, bubbles of air will penetrate the membrane.

The relationship between pressure and pore radius is given by the Laplace equation:

$$r_p = 2 \times \gamma / \Delta P \times \cos\theta$$

where r_p is the radius of a capillary shaped pore, γ is the surface tension at the liquid air interface, and θ the contact angle between the membrane material and the liquid.

On the basis of this formula, the maximum pore diameter can be calculated when ΔP is measured. The liquid type, the rate of pressure increase, and the pore length may all influence the results. Some typical results using water as the wetting medium are shown in Table 6.

This method can only be used to measure the largest active pores in a given membrane, and has become a standard technique used by suppliers to charac-

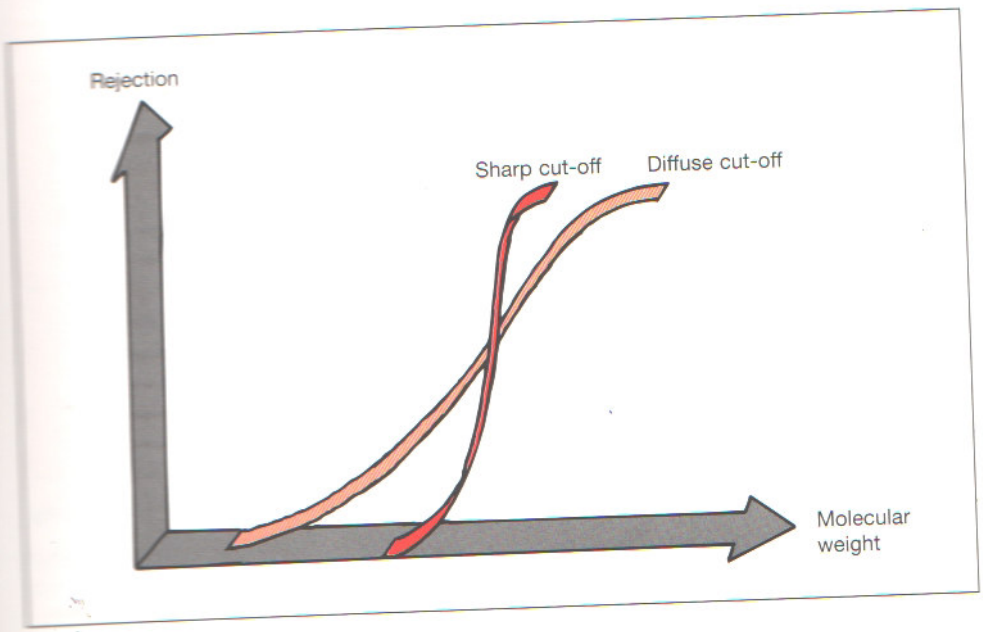


Figure 31: Rejection characteristics for UF membranes. The separation characteristics of membranes may vary from a very sharp cut-off value to a more 'diffuse' cut-off value. In order to achieve the best separation, membranes should be produced with the sharpest possible cut-off value.

Table 6:
The bubble-point method. Typical values using water as the wetting medium.

Pressure bar	Pore radius µm
0.14	10
1.4	1.0
14.5	0.1
145	0.01

terise the conventional dead-end micro-filtration membranes.

Molecular cut-off value

Most manufacturers use the 'cut-off value' to characterise UF membranes. Cut-off value is normally defined as that molecular weight which is 90% rejected by the membrane. Consequently, a cut-off value of 40,000 implies that all solutes with a molecular weight higher than 40,000 are more than 90% rejected.

Figure 31 shows a schematic comparison of a membrane with a sharp cut-off value and a membrane with a more diffuse cut-off value. It is usually desirable to have as sharp a cut-off value as possible in order to obtain the best possible separation.

The cut-off value is a useful tool to determine the most appropriate membrane for solving a specific separation problem. However, it must be realised that there are other parameters which influence the performance, such as the shape and flexibility of the macro-molecular solute, its interaction with the membrane material and last but not least fouling and concentration polarisation phenomena.
Table 7 illustrates the molecular cut-off concept for a range of different membranes, including the influence of the structure of the macro-molecules.

Table 7:
The behaviour of UF membranes on rejection of polymers.

Membrane *(All Amicon types)*	Globular protein	Branched polysaccharides	Linear, flexible polymer
XM 50	γ - globulin MW = 160,000 Albumin MW = 69,000		
PM 30	Pepsin MW = 35,000	Dextrane 250 MW = 236,000	
PM 10	Cytochrome C MW = 13,000	Dextrane 110 MW = 100,000	Polyacrylic acid MW = 50,000
UM 10	Bacitracin MW = 1,400	Dextrane 40 MW = 40,000 Dextrane 10 MW = 10,000	Polyethylene glycol MW = 20,000

Molecules above the horizontal line are fully rejected, whereas molecules below the line are partly rejected or able to fully permeate the membrane. The table illustrates the significance of the molecular structure. Linear and partly-branched molecules pass through the membrane much more easily than globular molecules

Temperature

The influence of temperature on membranes must be carefully considered in the operation of membranes and membrane systems. The following effects of temperature should be taken into account:

- Increase in temperature decreases viscosity by approximately 2.5% per degree centigrade, which increases the capacity of membranes for water solutions and most other media at the same rate
- Reduction in viscosity of viscous products due to increase in temperature reduces pressure drop which facilitates the operation
- Increase in temperature increases the rate of chemical reactions. This means that chemical attack on the membrane polymer and/or the support material through e.g. hydrolysis will increase with temperature
- Increase in temperature increases the degree of polymer chain mobility and decreases the tensile strength of the polymer. When the membrane is exposed to pressure, the polymer tends to creep, and this tendency will increase with temperature. This results in an irreversible compaction of the membrane which will change the membrane properties
- Increase in temperature during cleaning improves the efficiency of cleaning agents due to the decrease in surface tension and the increase in rate of chemical reactions
- Increase in temperature increases the killing rate of micro-organisms which is essential for efficient cleaning and sanitation of a membrane plant

All of these factors must be considered when choosing the most appropriate operating temperature and the most efficient cleaning programme.

Pressure

Since membrane filtration is a pressure-driven process, the influence of pressure on membrane performance must be recognised, and it can be summarised as follows:

- Increase in pressure increases flux rate to a certain point, depending on flow conditions and properties of the processed product
- Increase in pressure is required to overcome the osmotic pressure
- Increase in pressure decreases permeability of solutes
- Increase in pressure increases the irreversible creep of polymers and corresponding changes in properties

pH

The hydrolysis of polymers is controlled by pH and temperature. Since pH may vary considerably for different products, and since pH is a decisive factor in designing the cleaning procedures, it is necessary to know the pH limits within which the membrane can be treated without risking irreversible changes. Table 8 shows a list of recommended pH values for operating, and a maximum pH range for cleaning. Similar data are given for temperature and pressure.

pH also influences the structure of macro-molecules, the composition of organic and inorganic salts, the formation of calcium complexes, and many other properties of solutes in a solution which may influence flux rate, concentration polarisation and fouling.

Table 8: Cleaning and storage conditions for a range of membranes.

		Membrane type					
		CA[1]	NF[1]	HR[1]	GR[1]	FS[1]	RC[1]
Cleaning and short-term disinfection							
Temperature	°C	0-35	0-50	0-60	0-75	0-65	0-60
Pressure	bar	10	1-5	10	5	5	5
pH	%	2-8	2-11	1-12.5	1-13	1-11.5	1-11.5
NaOH[2]	%	-	0.05-0.1	0.2-0.3	0.5-1.0	0.1-0.2	-
EDTA[2]	%	0.5-1.0	0.2-0.3	0.5-1.0	0.5-1.0	0.3-0.5	0.2-0.3
Strong mineral acid[2]	%	-	0.1-0.2	0.3-0.5	0.3-0.5	0.3-0.5	0.3-0.5
Citric acid[2]	%	0.5-1.0	0.5-1.0	0.5-1.0	0.5-1.0	0.5-1.0	0.5-1.0
Chlorine	ppm	20[4]	0	0	200[3]	1,000[3]	20[3]
Hydrogen peroxide	ppm	1,000[4]	1,000[4]	500[5]	1,000[3]	1,000[3]	1,000[3]
Hot water/80	°C	-	-	+	+	+	+
Storage at room temperature							
Formaldehyde	ppm	5,000	5,000	5,000[6]	5,000	5,000	5,000
Sodium hydrogen sulphite	ppm	2,500	2,500	2,500	2,500	2,500	2,500

[1]NF/HR: thin film composite. GR: polysulphone. FS: flourpolymer.
RC: regenerated cellulose acetate. CA: cellulose acetate.
[2]pH limits dominate, so these concentrations should be adjusted to the right pH
[3]Maximum temperature 35°C (Plate and frame only)
[4]Maximum temperature 25°C
[5]Not to be used during first 24 hours of operation
Antifoam agents should be avoided

Organic solvents

Polymers used for membranes are almost all attacked by some solvents. As explained in the section about membrane manufacture below, the most common way to manufacture membranes is to dissolve the polymer in an organic solvent. Consequently, care must be taken when dealing with organic solvents or products containing organic solvents even in small quantities. Even though suppliers provide lists of the influence of organic solvents, they must be treated with caution since the polymer cast as a membrane with a high water content may react differently from the pure solid polymer. Information on the influence of organic solvents is usually scarce, and it is recommended that the manufacturer is consulted in each specific case. Ceramic membranes are resistant to most organic solvents.

Cleaning chemicals

The resistance of membranes to cleaning chemicals is essential for the practical utilisation of membrane systems. Table 8 gives a list of some of the more common cleaning and disinfection chemicals and the tolerance level for various membrane polymers. Today, many industries use formulated cleaning agents supplied by companies specialised in cleaning of industrial equipment and plants. Since the formulation of such cleaning agents is usually complex, and most frequently a trade secret of the manufacturer, it is necessary to test each individual cleaning agent in accelerated long term testing, in order to predict how the cleaning agent may influence a specific membrane.

To put this testing into perspective, the number of recommended formulated cleaning chemicals range from 20 to 40

for each manufacturer. The cleaning chemicals fall into the groups of acids, alkalis, enzymes, and chemical disinfection agents. They are either obtained as solids which need to be dissolved, or as concentrated liquids which need to be diluted prior to use.

The manufacturers of membranes usually have compatibility charts showing the tolerance of their membranes to specific commercial cleaning agents.

Membrane manufacture

Manufacture of synthetic membranes is based on a comprehensive range of very different techniques. The cellulose acetate membranes originally produced by Loeb - Sourirajan were based on the so-called *phase inversion* principle followed by *immersion precipitation*. At that time, no machines had been developed, and membranes were simply produced by dissolving the polymer (cellulose acetate) in suitable solvents (acetone, dimethylforamide, tetrahydrofuran), casting the solution in a thin layer (0.25 mm) onto a glass plate, leaving the glass plate in the open atmosphere for a limited time, and dipping (immersing) the glass plate into a water bath at a controlled temperature. After the solvents had been leached out and exchanged with water, the membrane was heat treated (cured) in a hot water bath in order to adjust the membrane selectivity. Obviously, this procedure contained a fairly large number of variables, and at that time most of the development was based on trial and error.

In addition to phase inversion - which today is the basis for the vast majority of membranes produced around the world - there are other techniques, amongst which the most important are *sintering*, *stretching*, *track-etching* and *coating*. Coating is a technique used in the preparation of thin film composite membranes. There are several different coating techniques, but *interfacial polymerisation* and *dip coating* are the most common.

In terms of membrane manufacturing, there are basically two distinctly different types of membrane configurations:

- Flat sheet configuration:
  - plate-and-frame
  - spiral-wound
- Tubular configuration:
  - conventional tubular. Diameter >10 mm
  - hollow fibre. Diameter 0.1-10 mm
  - hollow fine fibre. Diameter < 0.1 mm

Although the performance of flat sheet membranes and tubular membranes is similar, the procedure for manufacturing of membranes is quite different.

Flat sheets

Flat sheet membranes are used in plate-and-frame and spiral-wound systems. The method of manufacturing is as follows:

(1) *Chemical compound mixing*. The polymer is dissolved in a suitable mixture of solvents followed by addition of swelling agents. This is usually done in batch vessels, and the complete dissolution of the polymer will take some time due to the high viscosity of the final solution

(2) *Filtration*. After the dissolution of the polymer, the casting solution is filtered in order to remove any insoluble particles which may otherwise cause pin-holes in the surface of the membrane

(3) *Extrusion*. The casting solution is extruded onto the non-woven support paper which rests on a stainless steel conveyer belt pulled forward at the speed of extrusion. The casting solution is exposed to a controlled atmo-

sphere for a controlled period of time, allowing some of the solvents to evaporate. On leaving the chamber with the controlled atmosphere, the membrane passes into a coagulation bath of chilled water, where the solvents and swelling agents are washed out and exchanged with water. Finally, upon leaving the conveyor belt, the membrane is wound up - ready for further processing

(4) *Curing*. For some membranes the preparation process is completed after extrusion, while others - especially asymmetric RO membranes - need to be heat treated in a hot water bath at temperatures of 60-85°C for a certain period of time. This causes the membrane to shrink, and the surface layer to become more dense, which reduces the permeability of salts.

The manufacturing of flat sheet membranes as described above, is illustrated in Figure 32. The casting machines for extruding the membranes are usually manufactured by the membrane suppliers, and they may vary somewhat from one supplier to another.

Tubular membranes

The diameter of conventional tubular membranes is so large that they need to be supported, while in hollow fibre elements the diameter is so small that the fibre is self-supporting. This obviously means that different manufacturing techniques have to be used for manufacturing the membrane elements.

Figure 33 shows how tubular membranes are manufactured. The key element is the casting-bob assembly.

The film casting solution - which is prepared in the same way as described for flat sheet membranes - is fed under pressure from an overhead storage vessel. The casting solution is ejected through four perpendicular horizontal openings, uniformly placed around the space between the porous support tube and the casting-bob. When the tube is moved vertically, a film is cast on the inner side of the porous support. The tube is subsequently immersed in a coagulation bath where precipitation of the casting solution leads to the formation of the tubular membrane.

The tapered bucket-trailer shown in Figure 33 squeezes the casting solution into the voids of the support tube, it eliminates air bubbles and re-spreads the casting solution on the support surface.

After the formation of the membrane, water is pumped under pressure through the tubes, in order effectively to remove solvents and swelling agents and replace them with water.

In the preparation of fibre elements, spinning techniques - similar to those used in the textile industry - have been developed.

Figure 34 illustrates the manufacturing principles of the *dry-wet spinning technique*. A viscous polymer solution containing polymer, solvents and swelling agents is pumped through a spinneret. The viscosity of the casting solution must be high - in the order of 10,000 centipoise - and it must be carefully filtered in order to prevent blocking of the spinneret. The bore injection fluid is pumped through the inner tube of the spinneret. After a short residence time in a controlled atmosphere, the fibre is immersed into the coagulation bath, where the final membrane formation takes place. Following the coagulation bath, the fibre moves to a flushing bath where solvents and swelling agents are removed from the membrane and replaced with water. Finally the fibres are collected on a godet.
Melt spinning - a similar technique as used for manufacture of textile fibres - is

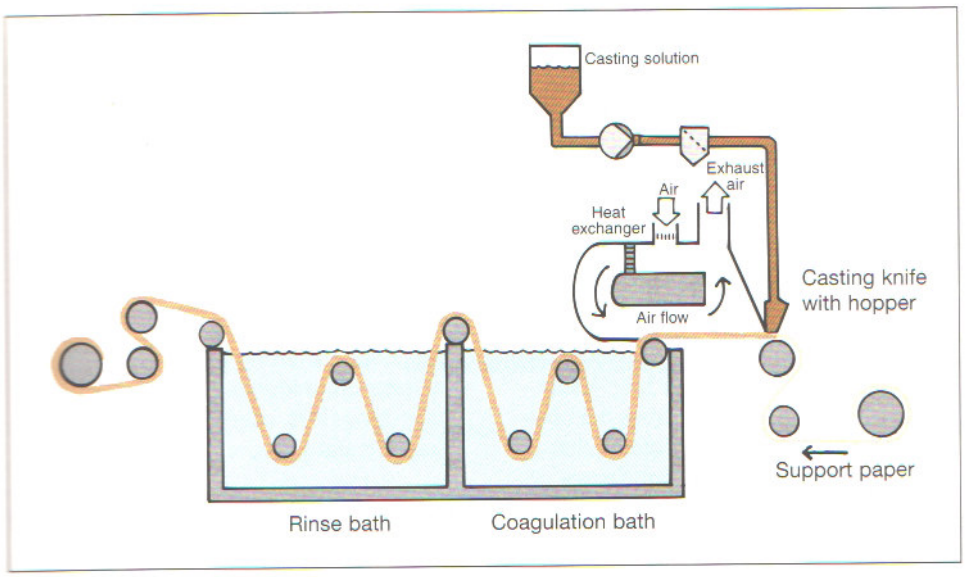


Figure 32: Production of flat sheet membranes. The casting machine produces membranes for spiral-wound and plate-and-frame membrane systems.

used in the manufacture of polyamide (nylon) based hollow fine fibres, where the dimension of the fibre is in the order of 40-50 µm, and the outside/inside diameter ratio is larger than 2. Such fibres act as a thick-walled pressure tube capable of withstanding the high pressures used in RO. The spinning rate in melt spinning is in the order of thousands of metres per minute, compared to the technique described above where the spinning rate is in the order of a few metres per minute.

Thin film composite membranes

The most successful technique for the manufacture of thin film composite membranes is the *interfacial polymerisation technique*. In this case, a polymerisation reaction occurs between two very reactive monomers at the interface of two immiscible solvents.

The process is illustrated schematically in Figure 35. The support layer, which is generally a UF or an MF membrane, is immersed in an aqueous solution containing a reactive water soluble monomer, mostly of the amine type. The soaked film (or fibre) is subsequently immersed in a second bath, containing a water-immiscible solvent, in which another reactive monomer - frequently an acid chloride - has been dissolved. These two monomers react to form a dense polymeric top layer. Heat treatment may be applied to accelerate and complete the interfacial reaction and to cross-link the

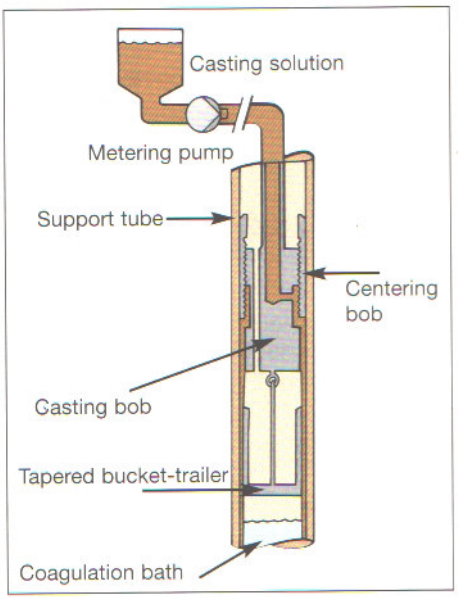


Figure 33: Production of tubular membranes. Casting bob assembly for casting integrally supported, tubular membranes.

polymer chains. Through this process, it is possible to form extremely thin polymer layers on top of the support in the order of only 0.25 µm.

Dip-coating is a simple technique for preparation of composite membranes with a very thin, but dense top layer. An asymmetric membrane in the form of a flat sheet or hollow fibre is immersed in a coating solution containing the polymer, pre-polymer or monomer usually at a concentration of less than 1%. When the membrane is removed from the coating bath, the coating material and the solvent adhere as a thin layer. Subsequently, the membrane is processed in an oven where the solvent evaporates and where the cross-linking takes place. This method is used for the production of certain RO, NF, gas separation, and pervaporation membranes.

Other methods

Sintering is a simple technique, allowing porous membranes to be manufactured from organic as well as inorganic materials. The method is based on pressing powders consisting of particles of a particular size, and sintering at elevated temperatures, depending on the material used.

Sintering is used for a wide range of materials, including polyethylene (PE), polytetrafluorethylene (PTFE), polypropylene (PP), stainless steel, ceramics, graphite and glass.

Especially sintering has been successfully used for the manufacturing of PTFE membranes. PTFE is not soluble in any organic solvent due to its high chemical and thermal resistance. It should be noted that the sintering technique is only

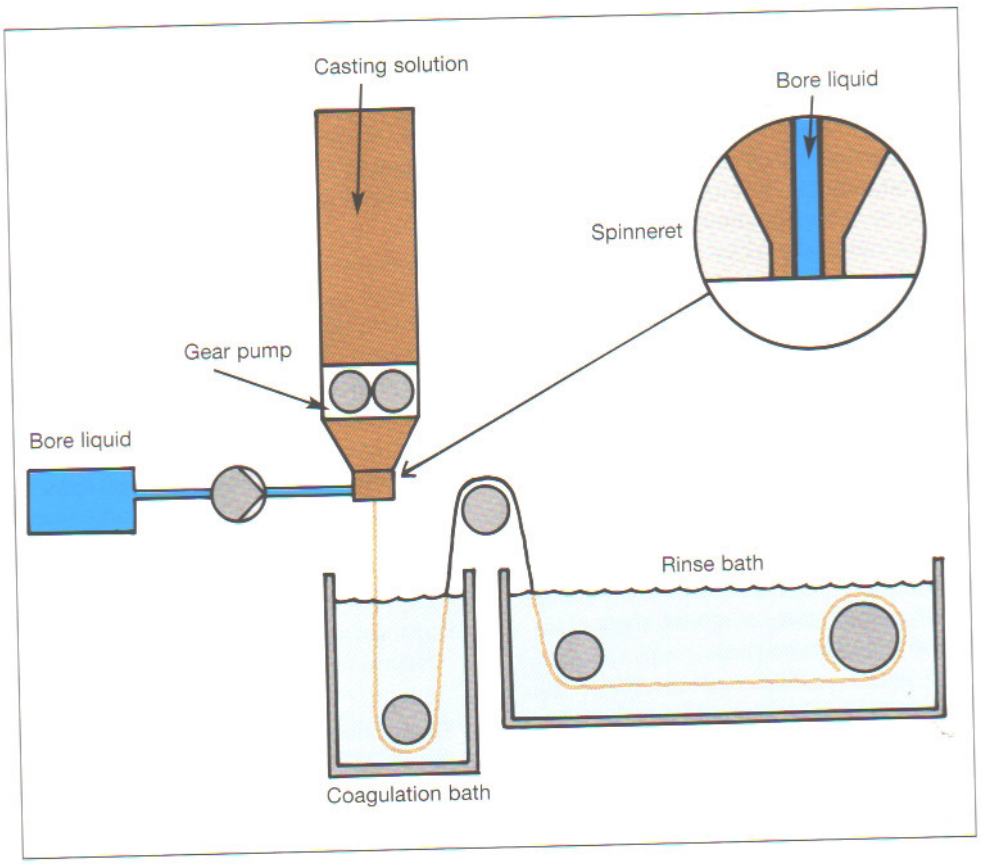


Figure 34: Casting/-spinning machine for the production of hollow fibre membranes.

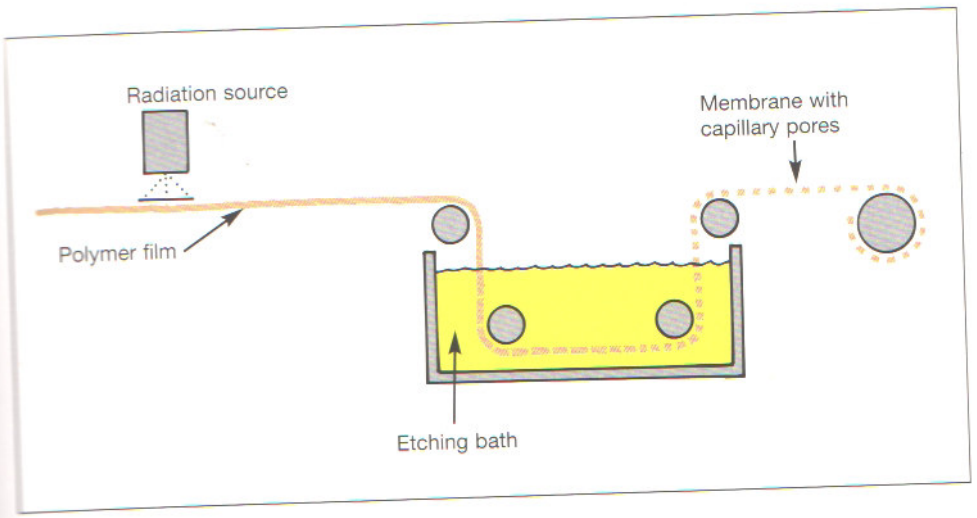


Figure 36: Preparation of membranes with uniform pores. Membranes are prepared by radiation of a polymer film followed by immersion in an acid solution.

used for the manufacture of MF membranes, since the structure of the membranes produced is symmetric in nature. The symmetric structure can be modified through coating of the surface, as in the case of ceramic membranes.

Stretching is sometimes used to modify extruded films made from PP, PE, or PTFE. By applying mechanical stress to the film, small ruptures occur, and a porous structure with pore sizes in the range from 0.1 to 3 µm is obtained. The porosity of such membranes is usually much higher than for membranes produced by sintering. This technique applies to MF membranes only.

Track-etching in a polymer film is caused by high energy particle radiation, applied perpendicularly to the film. The radiation damage the polymer matrix and create tracks. The film is then immersed in an acid or alkaline bath, and the polymeric material is etched away along these tracks to form uniform cylindrical pores with a very narrow pore size distribution. Pore sizes can range from 0.02 to 10 µm, but the surface porosity is fairly low. This method is used for the production of MF membranes from polycarbonate films. Figure 36 illustrates the preparation of porous membranes by track-etching.

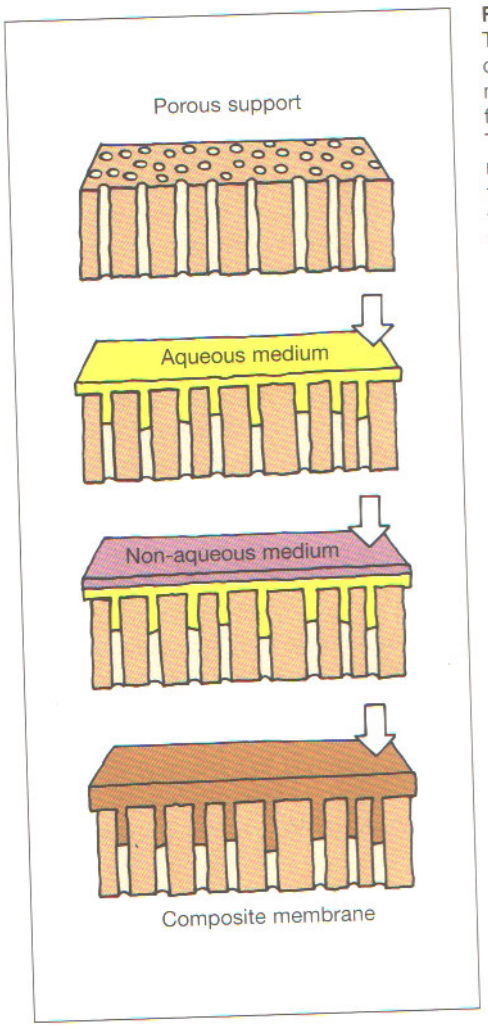


Figure 35: Thin film composite membrane formation. The mechanism of the 'in situ' formation of thin film composite membranes.

5 Resins

Resins have been known from ancient times but it is only since 1850 that the understanding of their constitution and formation has evolved. And it is only in the last few decades that the subject has expanded to become a true science from which extensive industrial applications have emerged.

Resin materials are still relatively expensive, and the efficiency of their utilisation and lifetime is essential to successful commercialisation. The main features a reliable industrial resin must fulfil can be summarised as follows:

- A hydrophilic structure of regular and reproducible form
- Controlled and effective exchange capacity
- Chemical stability
- Physical stability and mechanical strength
- Thermal stability
- Consistent and uniform particle size and effective surface area, compatible with the hydraulic design requirements for large scale plants

These requirements are, not surprisingly, quite similar to the requirements for industrial membranes. Even though good quality resins are available on the market today, there is still a large potential for improving them and reducing their manufacturing costs.

Ion exchange resins

Ion-exchange resins can be divided into inorganic based resins and organic polymer based resins. Today most resins are based on organic polymers, but the origin of ion-exchange resins is inorganic materials, and some of these are still used today e.g. as water softeners.

Inorganic resins. The mechanism of ion-exchange was first described in 1850 by two English soil chemists, H. S. Thompson and J. T. Way, who discovered that by treating a column of soil with a solution of ammonium sulphate, most of the ammonium was adsorbed, while the calcium content, originally contained in the soil, was released from the column. Their studies also revealed that the alumino-silicate fractions of soils were mainly responsible for the exchange properties, and that materials with exchange properties could be synthesised from soluble silicates and alum. Further investigations have proven that the finely divided clay minerals consisting of micro-crystalline alumino-silicates are directly responsible for the large exchange capacity of some soils. Consequently, natural fertile soil possesses an ion-exchange capacity. The addition of lime makes the clay soil more workable, because sodium in the clay is exchanged for calcium, giving a soil which retains less water and is less plastic.

Exchange reactions in soils are of immense importance for conveying nutrient elements to the root of plants, and for retention of fertilisers to be slowly released during the growing season of plants. Zeolites are naturally found minerals composed of alumino-silicates, with a crystal structure of well-defined channels and cavities, giving them a high ion-exchange capacity.

Artificially synthesised zeolites, also called permutits, have even better capacities than their natural counterparts. Unfortunately, they tend to decompose

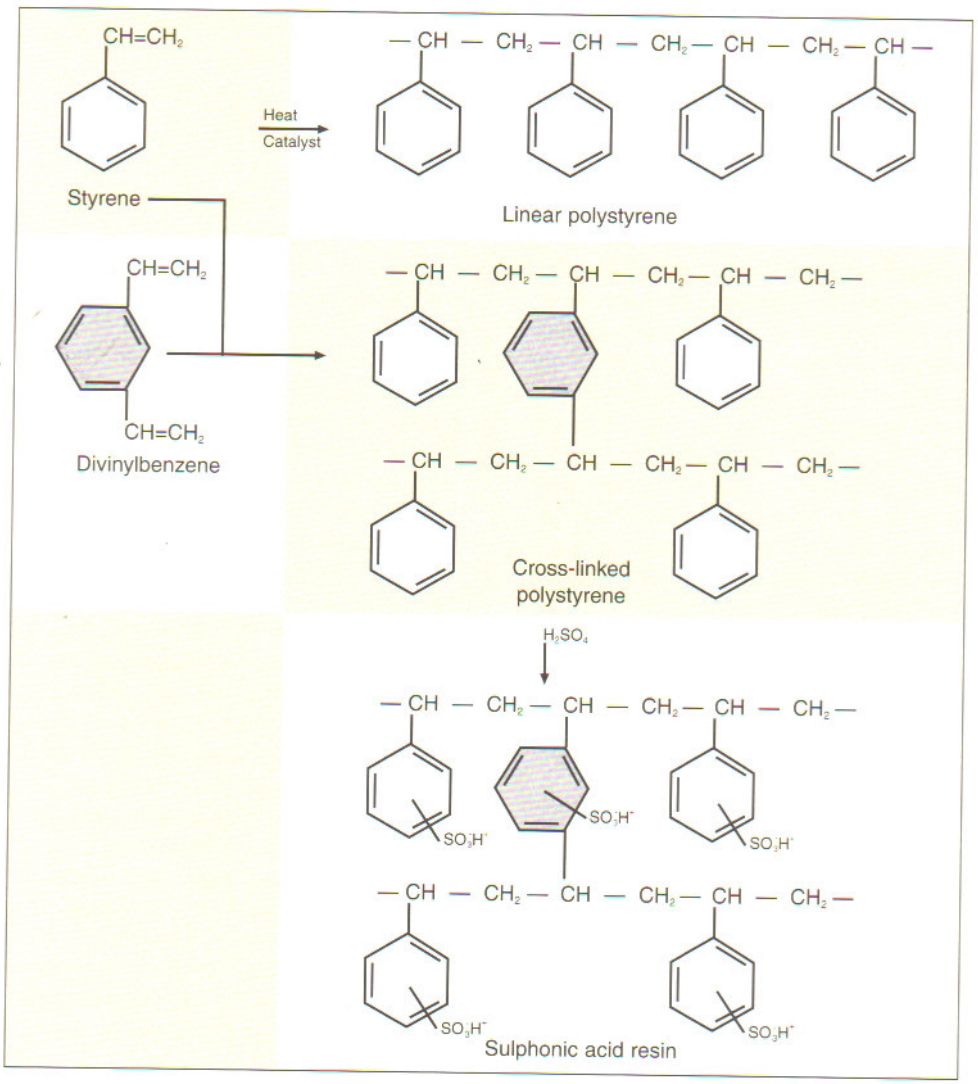


Figure 37: The chemical reactions in formation of cation exchange resins.

irreversibly in acid solutions, and today they are used mainly for water softening.

Organic resins. Most of today's cation-exchangers are based on co-polymerised polystyrene, cross-linked with divinyl benzene, and sulphonated with sulphuric acid to introduce sulphonic acid groups in the benzene nucleus. The reactions are illustrated in Figure 37. Essentially, anion-exchange resins are prepared by the same techniques, by incorporation of quaternary ammonium salts in the reaction in place of sulphuric acid.

The functional groups introduced can be varied in strength. In a weak cation-exchange resin, the sulphonic acid group ($-SO_3H$) is exchanged for a carboxylic acid group ($-CO_2H$). In weak anion-exchangers, the quaternary ammonium groups are substituted with di- and tri-substituted ammonium groups.

In industrial applications, efficiency and thereby financial benefits, are achieved by carefully selecting the resin with regard to the strength of the functional groups.

The porosity of polystyrene based resins depends on the degree of cross-linking in the resin structure, and this is determined by the proportion of divinyl benzene used in the manufacturing process. However, the selectivity of a highly porous resin is inferior to that of a less porous, highly cross-linked resin, and hence, in the manufacturing of general purpose resins, a compromise must be made between the conflicting requirements of high selectivity and high rate of exchange.

Ion-exchange materials can be made specifically for particular ions, e. g. for potassium, boron, and germanium by introducing particular functional groups in the resin. Such ion-exchangers are called specific ion-exchangers.

Chromatographic resins

Hydrophilic biopolymers play a dominating role as supporting materials for chromatography resins. These include neutral polysaccharides such as agarose, dextran, cellulose, and, to a lesser extent, starch.

They are traded under names like Sepharose, which is agarose in a cross-linked form, and Sephadex which is cross-linked dextran offered by English/-Swedish Amersham Pharmacia Biotech.

Life Technologies (USA) has launched a range of ion-exchange chromatographic resins based on regenerated cellulose that has undergone hydroxy-propylated cross-linking, which results in improved physical stability of the final matrix. A variety of ionic functional groups can be added to these matrices, which are available both in a granular form and as beaded resins. The resins are offered under the trade name of GibcoCel™.

The granular matrix is designed for use in stirred tank batch reactor systems where mechanical shear often reduces the economic life of the resin. The beaded matrix is better suited for column applications. These resins have been specially developed for separation of various types of proteins.

The Dow Chemical Company (USA) is marketing its resins under the name of Dowex Monosphere. Most of the Dow resins have structures based on styrene co-polymerised with divinylbenzene and include gel (micro-porous), as well as macro-porous resins. The Dowex Monosphere 99 is a gel type chromatographic resin developed primarily for separation of sugars and sugar alcohols.

More recently, the company Sepragen (USA) has launched a cellulose-based ion exchange chromatography material, designed for the radial flow chromatography columns. The new chromatography material is traded under the name of Sepragel®.

Sepragen has also developed a cation exchange resin based on a polymer composed of methacrylate moieties. It has a high stability profile and abundant ion-exchange sites that lead to high ligand binding capacities. The resin is traded under the name of SepraPrepS.

Synthetic polymers are used because of their superior physical and chemical durability. Amongst these are polyacrylamide beads offered by Bio-Rad under the trade name of Bio-Gel P.

Also inorganic materials such as porous glass, silica, alumina, and certain zeolites are used as base materials, because of their high mechanical and chemical stability and resistance to microbial degradation. Such materials are especially used in the field of immobilised enzymes.

Chromatographic resins work by temporarily adsorbing and slowing some components in a solution, while allowing others to pass. Small resin beads adsorb

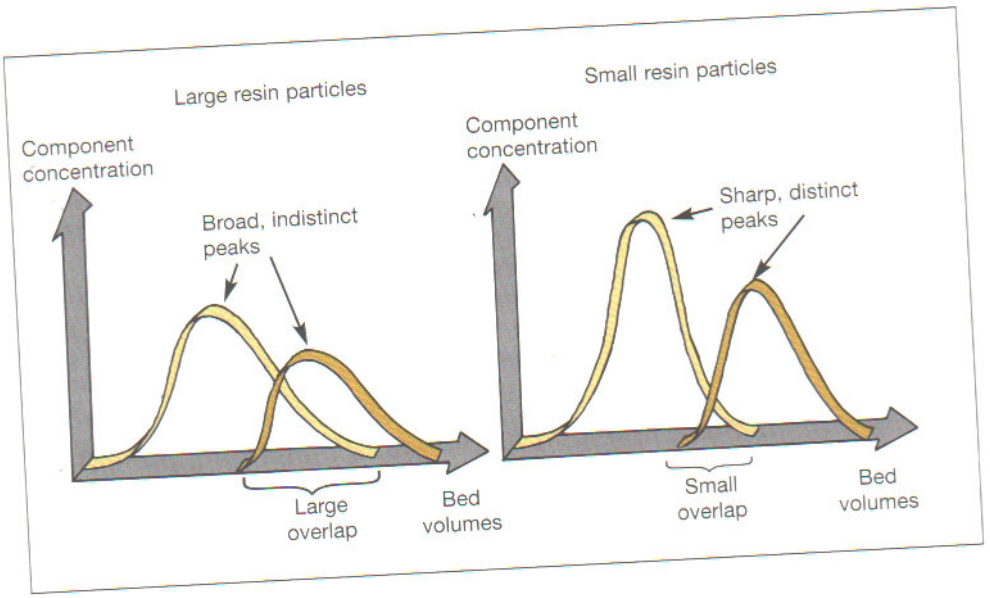


Figure 38: Comparison of the performance of large and small bead chromatographic resins.

and release components more quickly than large beads, resulting in more efficient and more distinct separation.

Figure 38 compares the separation efficiency of small versus large beads, showing a much larger overlap of the two peaks, representing two components to be separated, for the large particle resin.

The small bead resin also requires less water for elution, and consequently there is less water to be removed when the final product has to be prepared. Although smaller beads produce sharper separations, beads which are too small may cause excessive pressure drop through a column, reducing flow and production efficiency. Based on system design and operating conditions, there is an optimum bead size which is small enough to provide efficient and distinct separation, yet large enough not to cause excessive pressure drop.

Ideally, all resin bead particles would be of the same optimum size, but in reality most resins are produced with a relatively broad gaussian distribution of particle size. By modifying the manufacturing technique, it is today possible to produce resins with a very narrow particle size distribution, giving resins with improved separation characteristics.

Dow pioneered the use of uniform particle size resins already in the early 1980s. Originally, only gel type resins were produced according to this technique, but today the production technology is also applied for manufacture of macroporous resins.

No chromatographic applications are exactly the same. Each application requires some degree of customisation for optimum performance. Among the parameters that can be tailored are the following:

- *Mean particle size of the matrix.* This can be varied to meet specific flow property and/or binding capacity requirements
- *Degree of cross-linking within the particles.* This can be adjusted to alter the swell volume or improve the durability of the matrix
- *Degree of functional group substitution.* This is varied to achieve the

desired binding capacity for specific components

- *Alternative functional groups*. This is achieved through coupling of various types of active groups to the different types of matrices

By using these principles, it is possible to tailor resins for specific separation tasks. In combination with the new possibilities of going to industrial scale, it is predicted that the number of industrial applications will continue to increase in the future.

6 Polarisation and fouling

A major limiting factor in the use of membrane filtration processes is what is loosely termed as 'fouling' of the membranes. Fouling results in flux decline with the time of operation. It can be defined as the flux decline that occurs when all operating parameters, like pressure, flow rate, temperature and feed concentration are kept constant.

The fouling phenomenon has been regarded as the single most important reason for the relatively slow acceptance of membrane filtration processes in some industries, because of non-fulfilment of early promises in respect of performance.

The extent to which fouling occurs greatly depends on the type of separation task to be solved. Especially UF and MF are subject to severe flux decline, with process fluxes often decreasing to less than 5% of the pure water flux through the membrane.

Flux decline is caused by several factors amongst which the most important are:

- Concentration polarisation
- Absorption
- Gel layer formation
- Pore clogging
- Chemical changes in the membrane
- Physical changes in the membrane
- Bacteriological growth

Figure 39 illustrates the flux behaviour of typical UF/MF membranes as a function of time.

Resins may be subject to fouling in the same way as membranes. The individual resin particles may be covered with a fouling layer, precipitates may be formed due to changes in pH or ionic strength inside the pores of the resins, and the volume between the resin particles may be filled up with matter insoluble under the circumstances.

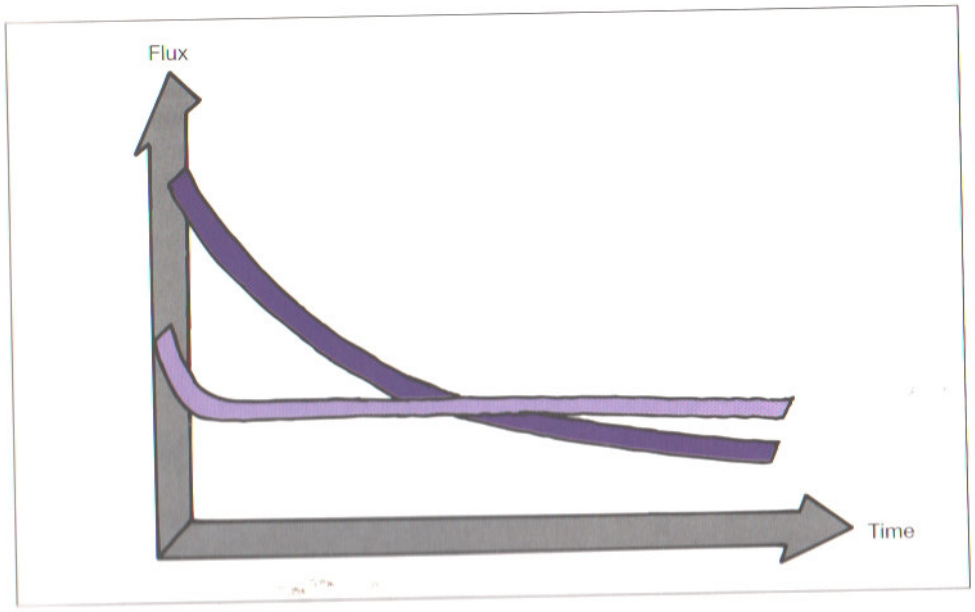


Figure 39: Flux behaviour of UF/MF membranes. High initial flux causes a rapid flux decline, whereas a limitation in the initial flux stabilises the performance over time.

Flux decline has a negative influence on the economics of any given process, and consequently, it is necessary to minimise and reduce flux decline as much as reasonably possible. In order to do so, it is necessary to understand the background and the mechanisms for various fouling phenomena.

Filtration versus cross-flow filtration

It should be noted that the membrane filtration processes, discussed here are distinct from the conventional filtration process discussed in Chapter 3.

In cross-flow filtration, the upstream fluid moves parallel to the membrane surface at a high velocity, and the downstream fluid moves away from the membrane, having lost a portion as permeate, which is collected on the low-pressure side of the membrane. The downstream fluid is usually circulated in order to reach the final separation objective. The velocity across the membrane is kept sufficiently high to prevent any build up of fouling material on the surface of the membrane.

In conventional filtration - in this context also called 'dead-end filtration' - the only outlet of the upstream liquid is through the filter, which causes a gradual build up of solids, eventually forming the filter cake.

Dead-end filtration and cross-flow filtration are compared in Figure 40.

Concentration polarisation

Solutions processed in membrane systems flow at high velocity across the membrane surface in a thin membrane channel. The flow pattern depends on the geometrical configuration of the channel system. The transport of a feed solution across the membrane surface will tend to cause solutes to accumulate on the membrane surface in the membrane channel. Because of the wall effect, the linear velocity across the membrane surface will always be lower at the interface than in the bulk solution.

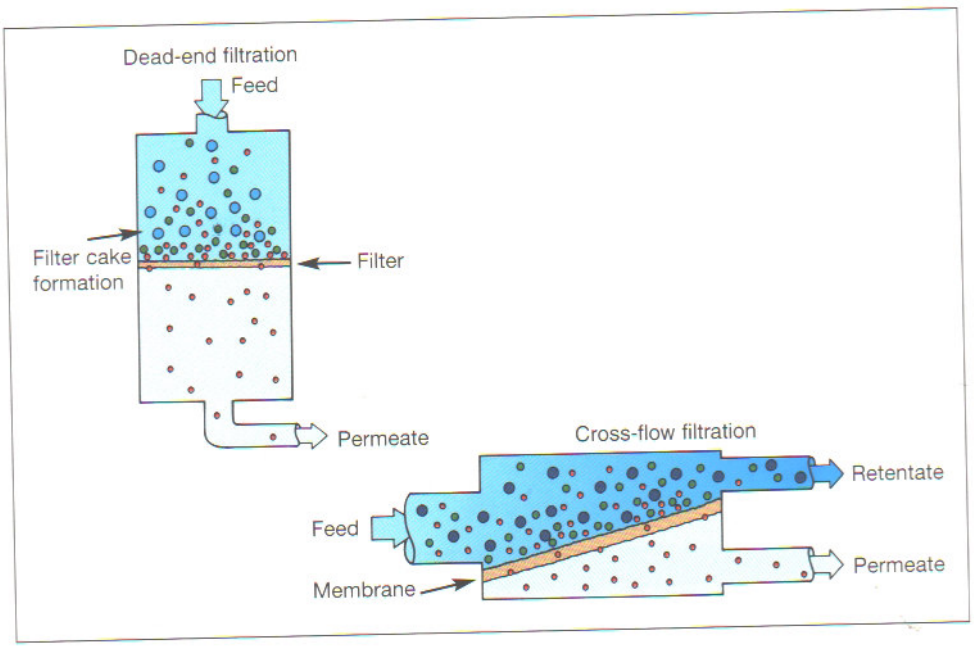


Figure 40: Dead-end filtration versus cross-flow filtration. In a dead-end filter, a filter cake is deposited on the surface, while in cross-flow filtration the membrane surface is kept clean through the sweeping action of the high-velocity feed liquid.

This means that a thin boundary layer exists where the exchange of solutes is poorer than in the bulk solution. The accumulation of solutes at the interface will continue until a degree of concentration is reached at which the back diffusion of solutes equals the solutes transported to the membrane surface by the flux. This can be expressed mathematically in the following way:

$$\frac{C_w - C_p}{C_b - C_p} = \exp (J_w/K)$$

or:

$$J_w = K \times \ln \frac{C_w - C_p}{C_b - C_p}$$

where

C_w = concentration at interface (wall)
C_p = concentration in permeate
C_b = concentration in concentrate (bulk solution)
J_w = solvent flux
K = mass transfer number

and where K depends on the geometrical configuration of the system, and the velocity of the liquid across the membrane surface. This phenomenon is called concentration polarisation, which more explicitly can be expressed in mathematical terms as:

$$CP = C_w / C_b$$

where

CP = concentration polarisation

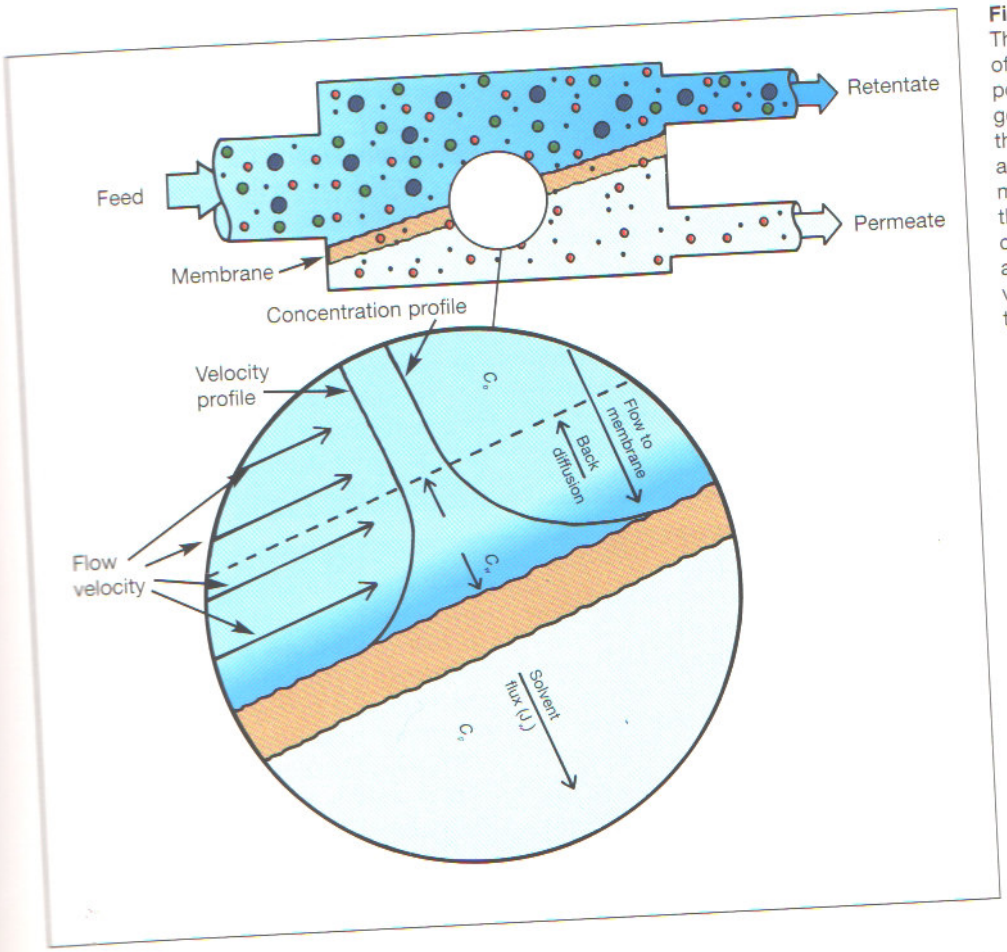


Figure 41: The formation of concentration polarisation is governed by the velocity across the membrane, the solute concentration, and the viscosity of the solution.

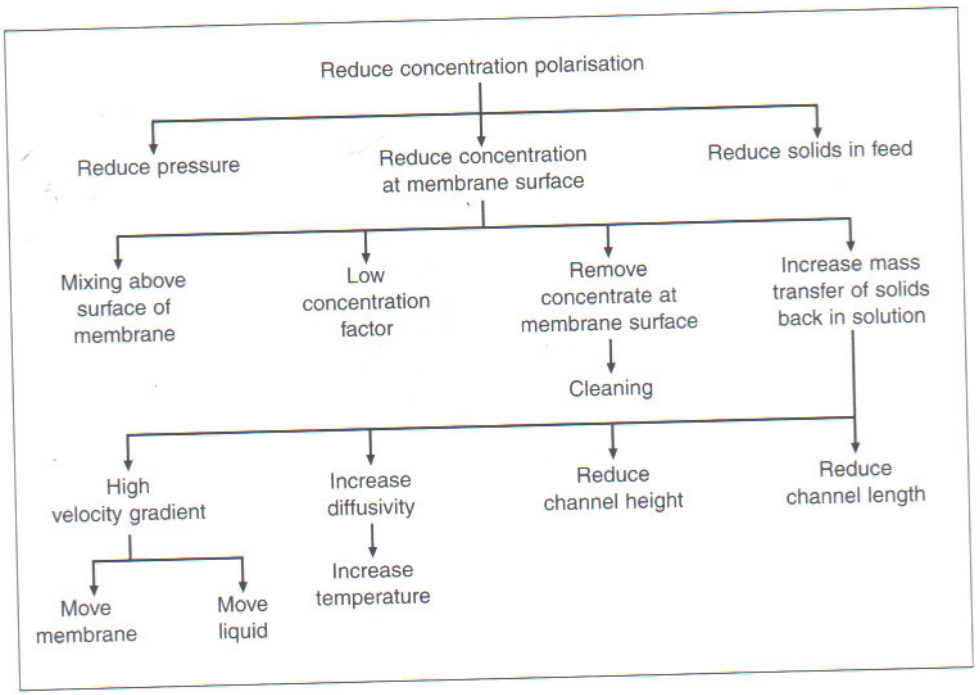


Figure 42: Reducing concentration polarisation. Controlling and minimising concentration polarisation is essential for the performance of a membrane system.

The consequences of concentration polarisation are very important for the operation of any membrane system, on any product, at any level of concentration, and can be summarised as follows:

- *Reduced retention.* Because of the increased solute concentration at the surface of the membrane, the actual retention will be lower than the intrinsic retention. This is generally the case for low molecular weight solutes such as salts.

- *Increased retention.* However, the retention can also be increased. This is especially true for mixtures of macro-molecular solutes, where concentration polarisation can have a strong influence on the selectivity. The higher molecular weight solutes that are retained completely form a kind of secondary or dynamic membrane, which will cause the rejection to increase for the lower molecular weight solutes.

- *Reduced flux.* The build up of concentration on the surface of the membrane increases the osmotic pressure far beyond the level in the bulk solution, and this, together with the formation of the secondary membrane as described above, will with time cause a decreased flux rate. This phenomenon is very pronounced for MF and UF, but of much less importance in gas separation, where concentration polarisation hardly occurs.

Figure 41 illustrates the build up of concentration polarisation in UF.

Figure 42 illustrates how concentration polarisation can be minimised in membrane systems by variations of different operating parameters. In the design of membrane filtration systems, these guidelines should always be kept in mind, in order to have a design which minimises the level of unavoidable concentration polarisation.

Laminar and turbulent flow

The influence of concentration polarisation is very pronounced in MF/UF processes. Consequently, it is important to seek ways to minimise the concentration polarisation as much as possible in order to maximise the flux rate and control the rejection of solutes.

In the light of the equations discussed above, this can be achieved by increasing the mass transfer number K. K is determined mainly by the diffusion coefficient, the flow velocity, and the temperature. This means that the flow velocity across the membrane becomes the key factor in determining the flux rate in a given membrane system.

Basically, it is possible to distinguish between two different flow patterns, i.e. *laminar* and *turbulent* flow. Figure 43 illustrates the difference between the two flow patterns in terms of velocity profiles.

Laminar flow is characterised by a parabolic velocity profile over the whole cross section, whereas in turbulent flow, the velocity in the cross section is constant, and only in the boundary layer near the wall is the velocity lower. Whether turbulent or laminar flow occurs is determined by the Reynolds number Re:

$$Re = \frac{\rho \times v \times d_h}{\eta}$$

where

ρ = density
v = flow velocity
d_h = hydraulic diameter
η = viscosity

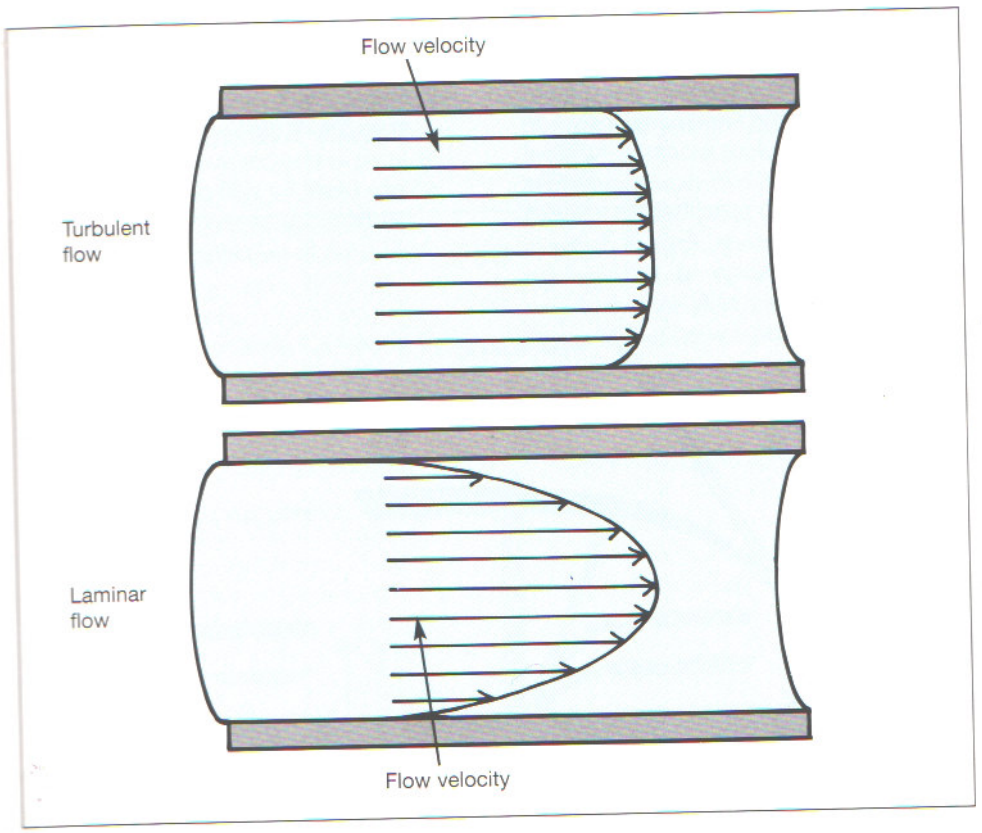


Figure 43: Turbulent versus laminar flow. The flow profile in the membrane channel is decisive for the performance of the membrane system.

Table 9: The effect of concentration polarisation on flux rates.

Membrane process	Level of influence	Origin
Reverse osmosis	moderate	K large
Ultrafiltration	strong	K small, J large
Microfiltration	strong	K small, J large
Gas separation	(very) low	K large, J small
Pervaporation	low	K large, J small
Electrodialysis	strong	-
Dialysis	low	J small

For an undisturbed flow through a straight pipe, the change from laminar to turbulent flow occurs at a Reynolds number of about 1,500-2,000.

There are, however, other methods for improving the mass transfer besides increasing the flow velocity, for instance through the use of turbulence promoters, breaking of the boundary layer by using corrugated channels, use of pulsating flow, use of flexible channels, and frequent changes in pressure (below the osmotic pressure). An increase in temperature will also generally decrease concentration polarisation, because of the increase in mass transfer coefficient. However, an increase in feed temperature also causes an increase in the flux, which opposes the effect of the improved mass transfer.

Table 9 summarises the causes and consequences of concentration polarisation in various membrane processes. As previously mentioned, the effect is very high in UF and MF because of the high fluxes and the low mass transfer coefficients resulting from low diffusion coefficients of macro-molecular solutes, small particles, colloids and emulsions.

The effect is less severe in RO due to lower fluxes and higher mass transfer coefficients. In very rough terms, the mass transfer coefficient in RO for low

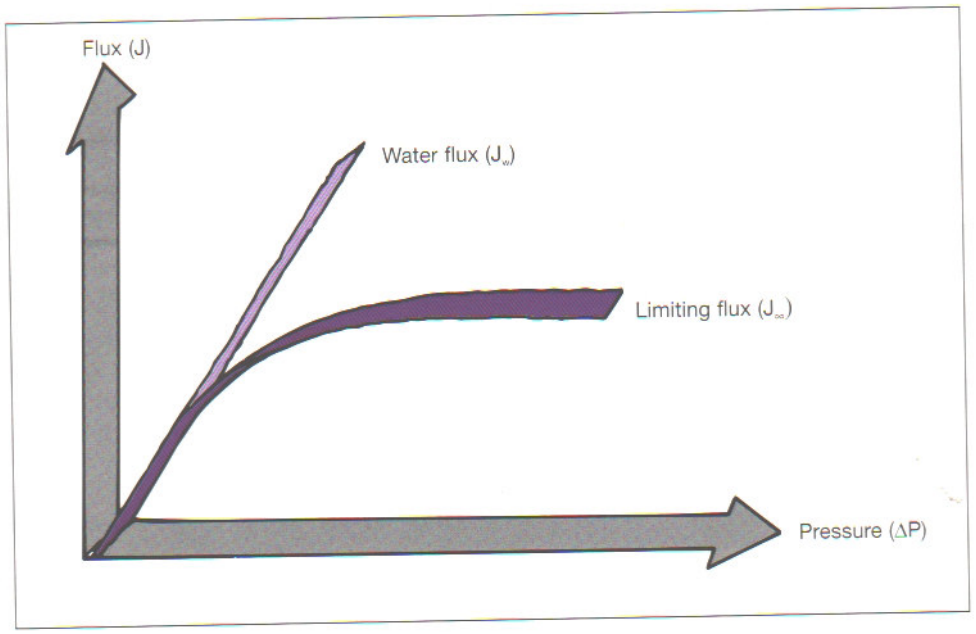


Figure 44: Flux versus pressure. Even though an increasing pressure increases the flux rate for pure water solutions, it is in practice limited by the nature and concentration of the feed solute.

molecular weight compounds is 10-100 times higher than for macro-molecular solutions in UF and MF.

In gas separation and pervaporation, the effect of concentration polarisation is very low, and can almost be neglected due to low fluxes and comparatively high mass transfer coefficients.

In dialysis, the effect of concentration polarisation is low because of the low fluxes and the relatively high mass transfer coefficients of low molecular weight compounds.

In electrodialysis, the effect of concentration may become more severe than in conventional dialysis.

An effect of concentration polarisation is clearly demonstrated in the analysis of flux behaviour as a function of pressure in UF. Generally, the pure water flux is directly proportional to the pressure applied as indicated in Figure 44. When solutes are added, the behaviour becomes very different. The flux increases with pressure but only to a certain point. The flux obtained at this point is called the limiting flux (J_∞) and can be expressed in the following equation, assuming 100% rejection of the added solute:

$$J_\infty = K \times \ln (C_w/C_b) = K \times \ln C_w - K \times \ln C_b$$

If the mass transfer coefficient is increased, for instance through an increase in flow velocity and keeping the solute concentration at a constant level, the limiting flux will also increase. If the mass transfer coefficient is kept constant and the concentration of the solute is increased, the limiting flux will decrease. These relationships are illustrated in Figure 45.

Gel layer formation

When the concentration polarisation of macro-molecules increases, a point is reached where the concentration at the membrane surface reaches the so-called gel concentration, and a gel layer is formed at the surface of the membrane. This gel layer can be depicted as a highly swollen fouling layer, comprising a three-dimensional cross-linked structure. At this point, the flux will reach zero, which basically means that the filtration process stops.

In practice, this means that the capacity of a UF plant cannot go beyond a certain level when macro-molecular solutes are being processed. However, a variety of factors will influence the ease and speed at which the gel concentration level is reached, like the surface properties of the membrane, the flow conditions in the flow channel, temperature and viscosity.

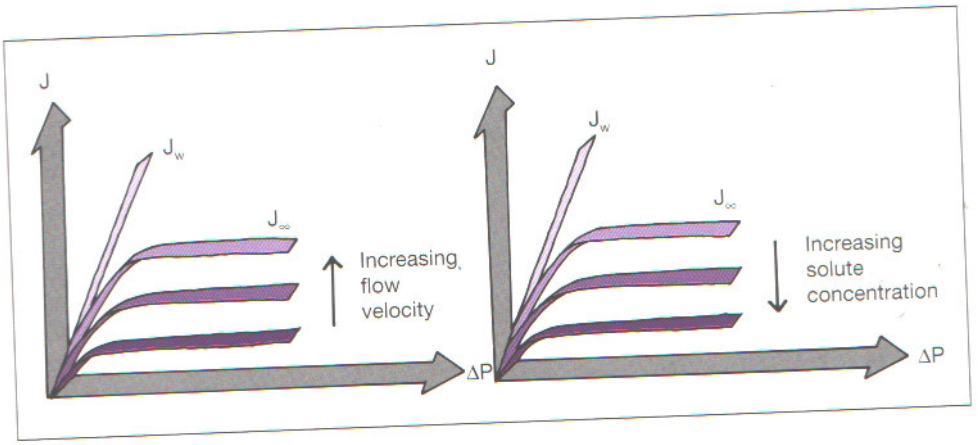


Figure 45: Flux versus flow velocity and solute concentration. Increasing flow velocity increases flux rates, whereas increasing solute concentration has the opposite effect.

Table 10: Gel concentrations of different products.

Product	Gel concentration %
Agar	2-5
Pectin	3-4
Carbowax 20 M	8
Casein	15
Bovine serum albumin (BSA)	25
Egg white	40
Red blood cells	45
Whey protein	60
Styrene butadiene latex	70

Some data for gel concentrations are shown in Table 10.

Membrane fouling

The performance of membrane filtration plants is hampered by polarisation phenomena and gel layer formation, meaning that the flux after a given time is always less than its original value. Even though concentration polarisation phenomena are reversible, it is commonly observed that the flux continues to decline with time. Such continuous flux decline is the result of membrane fouling, which can be defined as the deposition of retained particles, colloids, emulsions, suspensions, macro-molecules, salts, etc. on the membrane surface, and/or in the porous structure of the membrane. There are roughly three types of basic fouling materials to consider:

- Organic precipitates: macro-molecules, biological substances
- Inorganic precipitates: calcium salts, metal hydroxides
- Particulates: dirt, clay, silt

There are a number of ways of measuring the various fouling indices, and there are ways to model fouling. This book will only address the question of how fouling can be reduced or eliminated:

- *Pre-treatment of feed solution.* pH adjustment, addition of complexing agents, chlorination, addition of hydrogen peroxide are some of the chemical pre-treatment methods. Heat treatment is used to prevent bacteriological growth, but it is also a method for stabilising e.g. calcium salts.

  Filtration using conventional filters in their various forms is used to remove particles down to a particular size, in the same way as separators are used to remove emulsified fat. To some extent the removal of particles depends on the membrane filtration system used. Thin channel systems are more sensitive to particle fouling, since the particles may plug the entire flow channel. Tubular systems, on the other hand, are less susceptible to plugging.

  Generally, the best way to obtain an optimal flux is correct pre-treatment:

- *Membrane properties.* A change of membrane properties can reduce fouling. Fouling with porous membranes (MF/UF) is generally much more severe than with dense membranes (NF/RO). Furthermore, a narrow pore size distribution can also reduce fouling. The use of hydrophilic rather than hydrophobic membranes is another way to reduce fouling. Generally, proteins absorb more strongly at hydrophobic surfaces and are less readily removed than at hydrophilic surfaces. Charged membranes (negatively) may also help to diminish fouling, especially in the presence of negatively charged colloids.

- *Module configuration.* The module configuration has a significant effect on fouling. High flow velocities in thin flow channels seem ideal for most applications, provided particles which can plug the channels can be avoided through proper pre-filtration. The use of various kinds of turbulence promoters will also reduce fouling, but care should be taken that they do not trap particles or fibres contained in the feed.

  Recently, the so-called dynamic membrane module has been introduced, utilising the centrifugal force to reduce concentration polarisation and fouling. Another attempt to minimise fouling is the oscillating membrane module which has given excellent results on some specific products. For more information see Chapter 8.

- *Process conditions.* Changing some of the processing parameters like temperature, cross-flow velocity and pressure may have a significant effect on plant performance. Sometimes, there may be a choice as to where in a process it is most feasible to install the membrane filtration system.

- *Cleaning.* Although the above methods reduce fouling, cleaning in some form or another usually cannot be avoided. The frequency with which a membrane system needs to be cleaned may vary considerably from application to application. This very important aspect of membrane filtration will be addressed in more detail in Chapter 12.

7 Transport through membranes

So far, the membrane has been looked upon as a 'black box' having certain characteristics. But what happens inside the membrane itself when it is exposed to the various conditions described for the individual processes?

Transport through membranes has been - and still is - a subject of thorough investigation by many research organisations all over the world. A wide range of models have been proposed for each separation process, and attempts are continously made to find models which can encompass several of the filtration processes.

It is beyond the scope of this book to review these various models, and readers are referred to the very comprehensive literature on this subject. The following is an 'ultra-brief' review of the most basic concepts relating to transport through membranes.

As previously stated, membranes can be divided into two distinctive groups: porous and non-porous.

In order to describe transport through a porous membrane or a non-porous membrane, two contributions must be taken into account: the diffusional flow (v) and the convective flow (u). The flux (J_i) of a specific component (i) through a membrane can be described as the product of velocity and concentration (C_i) by the following equation:

$$J_i = C_i \times (v_i + u)$$

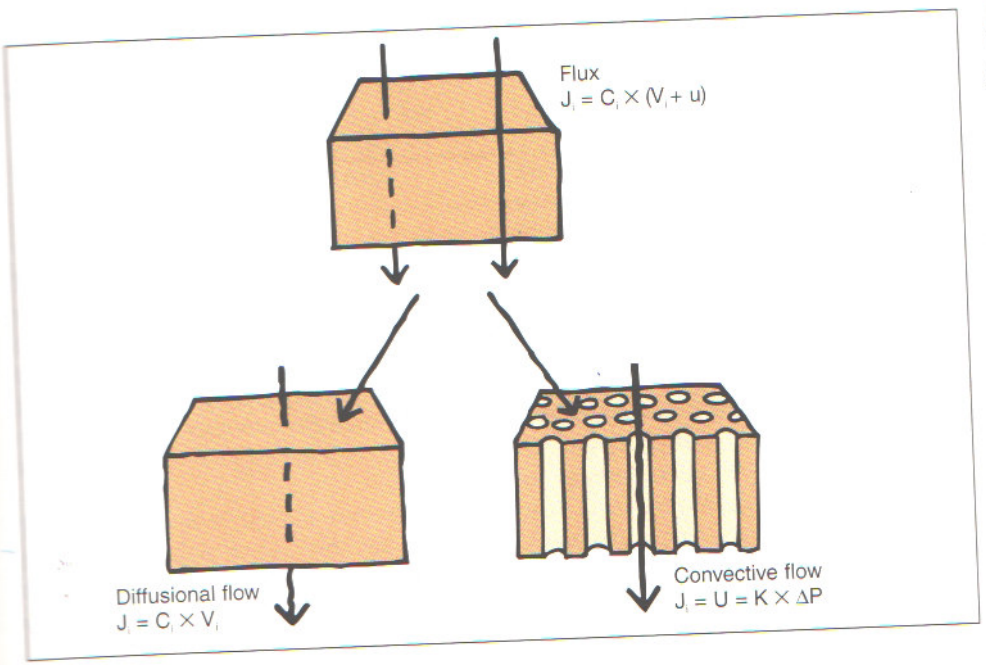


Figure 46: While convective flow is characteristic of porous membranes, diffusive flow controls the transport through non-porous membranes. In most cases, the transport is governed by a combination of the two.

The contribution of the convective flow is the main term in any description of transport through porous membranes. In non-porous membranes however, the convective flow term can be omitted, and only the diffusional flow contributes to transport of solutes through the membrane. This is illustrated in Figure 46. As far as extreme cases are concerned, it can be stated that transport in porous membranes occurs by convection and in non-porous membranes by diffusion. However, in going from porous to non-porous membranes, an intermediate region exists where both contributions have to be taken into account.

Transport occurs through the pores in porous membranes rather than the dense matrix, and parameters like pore size distribution, porosity, and pore dimensions are very decisive. The selectivity of such membranes largely depends on the difference between pore size and particle size.

In dense membranes, a molecule can only permeate if it dissolves in the membrane. The extent of such solubility is largely determined by the affinity between the polymer and the component transported through the membrane. Because of the existence of a driving force, the solute is then transported from one side of the membrane to the other via diffusion. Selectivity of such membranes is mainly determined by differences in solubility or differences in diffusivity. In this respect, there are large differences between gaseous and liquid permeants, since interaction between polymers and gasses in general is low, whereas strong interaction exists between polymers and liquids. This interaction between polymer and permeant may ultimately cause the polymer network to swell, which again can have a significant effect on the transport properties of the membrane.

8 Membrane systems

So far, the emphasis has been on the membrane, its characteristics and performance. In order for the membrane to function, and in order to be able to build large industrial plants with hundreds and thousands of square metres of membrane surface area, it is necessary to build the membrane into a system providing the following features:

- Sufficient support for the membrane at the required pressure
- A flow channel which brings the feed in intimate contact with the membrane
- A flow channel which enables flow at high shear rate across the membrane
- Unhindered permeate flow
- Easy membrane exchange
- Easy detection and isolation/-exchange of leaking membranes
- Parallel/serial coupling of membranes with uniform distribution of flow
- Handling of a range of viscosities
- A system sufficiently compact for the intended use
- A system which can cope with the requirements for sanitary design for the actual application, allow for proper cleaning and secure final product quality

The smallest entity of the membrane which can be exchanged is normally called a module or an element. In order to build large systems, such modules are serial/parallel coupled to provide the membrane area required to handle a specific job.

This chapter will review the various membrane module designs and the design of complete systems is addressed in Chapter 12.

There are several ways in which a membrane module can be designed in order to fulfil the demands described above, but basically all designs can be grouped into the following configurations:

- *Tubular:*
  - hollow fine fibre
  - hollow fibre
  - tubular
- *Flat sheet:*
  - spiral-wound
  - plate-and-frame
- *Other:*
  - parallel leaf
  - dynamic
  - oscillating
  - ceramic

The design of membrane modules has many similarities to the design of heat exchangers, where the requirements are to provide heat transfer, and establish heat transfer surfaces in a compact form, in intimate contact with the feed under flow conditions and giving an optimal heat transfer coefficient.

The early developments of membrane systems were mostly tailored towards future, high-capacity desalination plants for sea water, and this triggered the design of the hollow fine fibre system, which is perhaps one of the most remarkable developments. The values in Table 11 illustrate the influence of the tube diameter on the packing density. Hollow fine fibres have a fibre diameter of approximately 40 - 50 µm which will give a packing density of 36,000 m^2/m^3. Another unique development was the spiral-wound system, which is probably the most widely used system in the world today.

Table 11: Packing density of tubular membrane systems.

Tube radius mm	Surface area per volume m^2/m^3
5	360
0.5	3,600
0.05	36,000

Hollow fine fibres

Hollow fine fibres were originally designed for high-pressure RO desalination of sea and brackish water. The original system was developed by the American company DuPont, and the membrane modules were called 'Permasep' permeators.

The membrane fibres are spun from polyamide (nylon) in diameters ranging from 25 to 250 µm with a wall thickness of 5 to 50 µm. The design is a shell-and-tube configuration similar to single-end heat exchangers. The fibres are potted in a special epoxy resin, which is also used as the tube sheet. The feed enters the shell side near the head of the equipment, and the concentrated brine leaves from the other end. Water permeates from the outside of the fibre to the inside, through the fibre wall. Product water inside the hollow fibres leaves the system counter-current to the flow of the feed in the shell. The modules are designed to withstand pressures up to 70 bar.

Hollow fine fibres are also used for gas separation and for pervaporation. In pervaporation, the inside-out concept is used in order to avoid too high pressure losses on the permeate side. Figure 47 shows the principle design of the hollow fine fibre module.

Hollow fibres

Hollow fibres - sometimes also called capillary tubular modules - are primarily designed for UF and MF. The design was pioneered by Amicon Corporation in the USA.

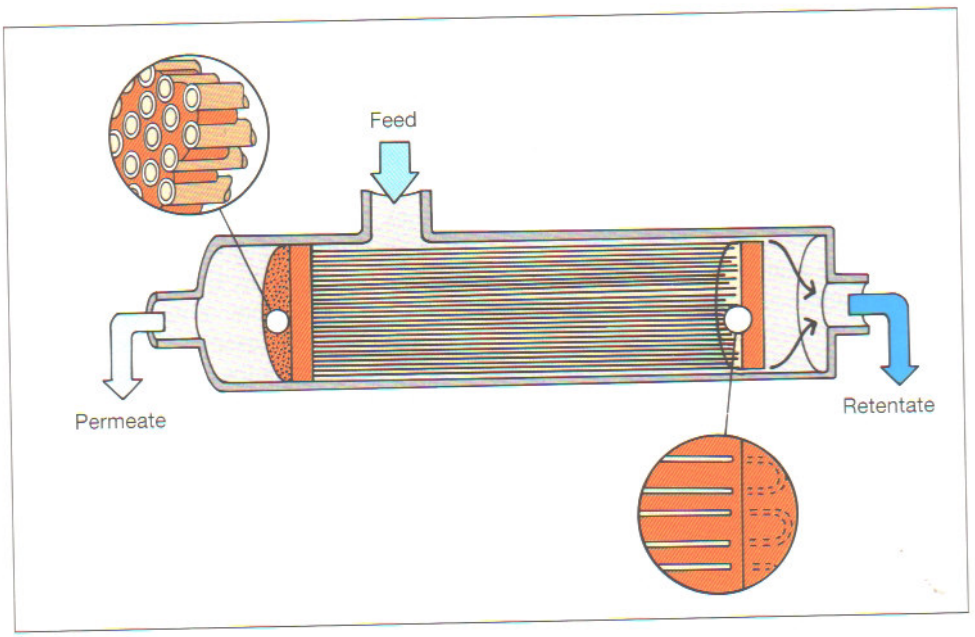


Figure 47: The hollow fine fibre module (HFF). This module was one of the pioneers in RO and was developed by DuPont based on nylon fibres.

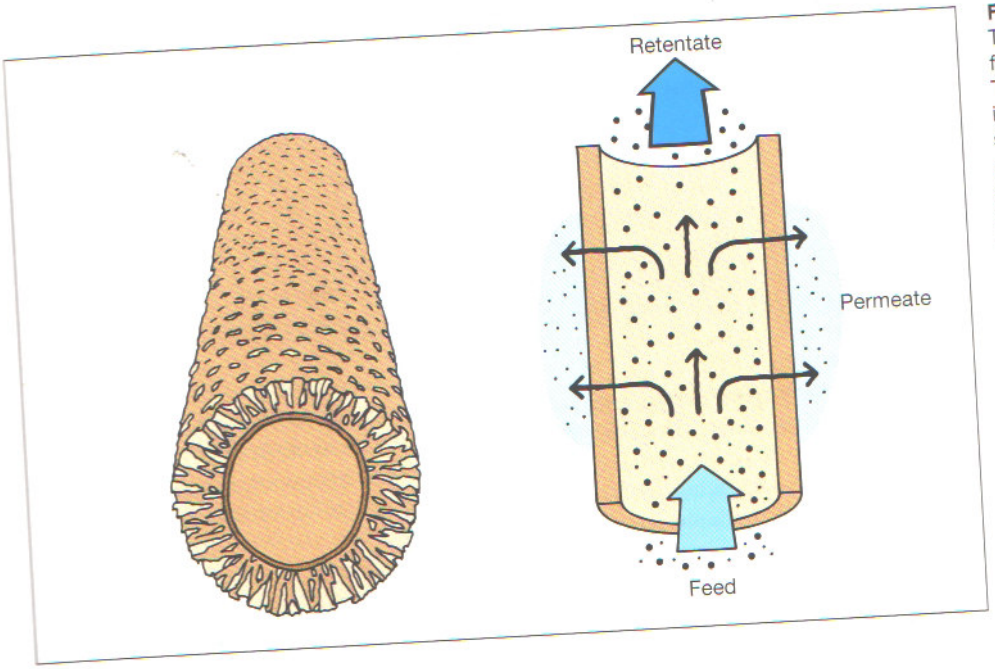


Figure 48: The hollow fibre system. The pioneer in UF systems, originally developed by Amicon Corp.

The membrane is in the form of a self supporting tube, with the dense skin layer on the inside of the tube. The diameter of the fibres may range from 0.2 to 1.25 mm. Bundles containing 50-3,000 individual fibres are sealed into a shell of plastic material in a shell-and-tube arrangement, and potted in each end with epoxy resin or similar material. The cartridge shell may be constructed from a clear see-through material like PS. Each module (cartridge) is equipped with a feed inlet, a concentrate outlet, and permeate outlets at each end of the cartridge. Cartridges for industrial applications are normally 3 inches (76.2 mm) in diameter, 110 cm in length and contain up to approximately 5 m^2 membrane area, depending on the fibre diameter.

It is also possible to make fibres with the active skin layer on the outside surface of the fibre. In this case, the feed solution enters the cartridge on the shell side, and the permeate is collected from the inside of the fibre. Due to the self supporting structure of the fibre, there is a maximum limit for operating pressure, usually in the range of 2-4 bar.

The small tube diameter and the high packing density make the fibres susceptible to plugging, and in order to prevent this, the feed has to be filtered with a 100 µm filter as a minimum requirement. A considerable advantage is the back flushing capability of the hollow fibre, which is also due to the self supporting fibre structure. This improves the possibilities for efficient cleaning of the membranes.

Figure 48 illustrates the design of the hollow fibre system.

Tubular

In the late 1960s, Havens Industries of San Diego, California, pioneered the successful commercial development of RO units using the Loeb-Sourirajan CA membrane in a tubular configuration. The units were based on a ½-inch tubular filament-wound porous fibre glass tube, and the membrane formed an integral part of the tube by actual bonding to its internal surface. The tubes had a maximum length of 8 feet. A maximum

of 18 tubes were assembled in one unit surrounded by a shroud for collection of permeate. Havens designed a machine for high speed manufacture of the tubes, which had a burst pressure of 350 bar. The intention was to be able to produce large quantities of tubes at a relatively low cost.

It was, however, Koch Abcor of Wilmington, Massachusetts, and Paterson Candy International (PCI) in the UK, who brought the tubular system into commercial industrial use. Koch Abcor uses 1-inch tubes 10 feet long for UF, while PCI uses ½-inch tubes 3.66 m long. Today there are a wide range of dimensions available to suit specific needs and applications.

RO modules are usually based on perforated stainless steel tubes, while UF modules are usually based on plastic support tubes made from PVC, polypropylene and similar materials.

A number of tubes are assembled in a permeate collecting shroud with end caps, providing a serial/parallel configuration of the individual tubes. The membranes are cast onto a tube of support paper, which is fitted into each individual tube. This reduces the cost of exchanging the membranes, because a complete exchange of the entire tube is avoided.

In comparison with the fibre systems, the tubular system is very robust and less sensitive to fouling. Consequently, less pre-treatment is required, and larger particles can be accepted in the feed. The larger diameter tube, however, requires more liquid per membrane area which increases dead volume and results in higher consumption of energy and cleaning chemicals. Treatment (both RO and UF) of juice with its content of particles and fibres is a good example of the unique properties of the tubular system.

Figure 49 illustrates the tubular system.

Spiral-wound

The spiral-wound system was originally designed by Gulf General Atomic of San Diego, California, and was originally known as the ROGA (Reverse Osmosis General Atomic) module.

The module consists of one or more leaves wrapped around a product water take off tube (permeate collecting tube). The leaves consist of the membrane, a porous permeate collection side backing material, and a feed channel spacer. The

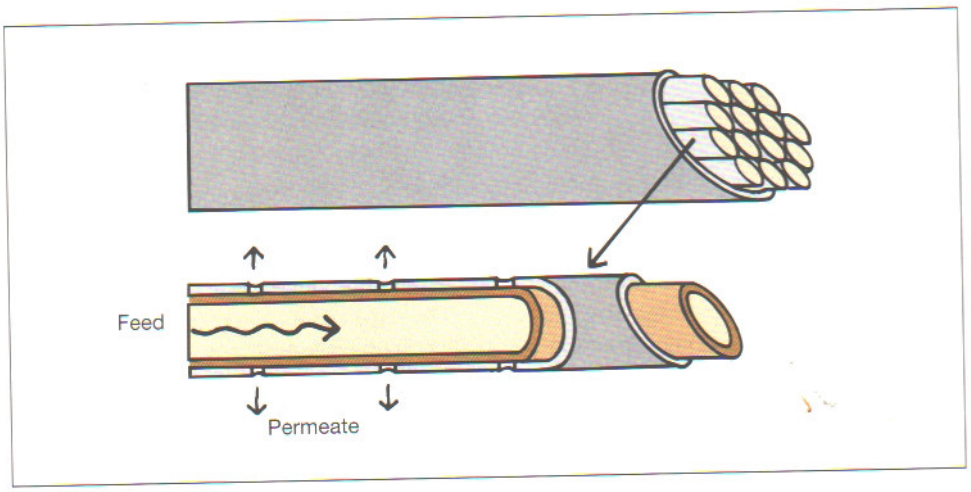


Figure 49: The tubular system. The inventor was Havens Industries. Today, there are a large number of manufacturers.

Element diameter	Element length	Membrane area per element		
inch	inch	30 mil spacer m²	50 mil spacer m²	80 mil spacer m²
3.8	33	5.5	4.2	2.5
3.8	38	7.0	5.6	3.7
6.3	38	17.0	14.0	8.0
8.0	40	36.2	26.0	-

Table 12: Typical spiral-wound element sizes.

membrane is bonded along the two sides, at the end, and around the permeate collecting tube, forming a sealed envelope that encloses the permeate backing material, except at the permeate collecting tube end which is open. The feed channel spacer is placed on top of the membrane, and the leaves are then wrapped around the permeate collecting tube to form a cylindrical element.

The element is placed in a snug fitting cylindrical pressure vessel. The feed enters at one end of the vessel, flows axially through the module in the passage provided by the course feed channel spacer, and out at the other end. Permeate is collected in the permeate backing material inward to the central permeate collecting tube. Depending on the capacity of a membrane for a given product, a spiral may have a different number of leaves. If the leaf becomes too long, an undesirable pressure drop may be created in the permeate collecting system.

There are two versions of spiral-wound elements. The original spiral is covered with a layer of fibre glass and is used for water treatment and water desalination. For such applications the high-pressure tubes are usually manufactured in fibreglass reinforced epoxy.

The other type is the sanitary spiral, where the spiral, after having been wound up, is wrapped in a sleeve of channel spacer material fitting the high-pressure tube closely. For sanitary applications it is common to use stainless steel high-pressure vessels.

The high-pressure vessels may contain as many as six standard size spiral-wound elements placed in a serial arrangement in which the elements are joined together with specially designed interconnectors. Furthermore, it is necessary to place so-called anti-telescoping devices (ATD) after each element in the flow direction, in order to prevent the spiral from telescoping - especially under the high pressure losses which may occur when treating products with high viscosity.

Originally the spirals were designed for water treatment only. A large number of improvements have been made over the years to develop a spiral suited for more difficult applications. High viscosity products require a spiral with a wider flow channel, and this is obtained by using a wider spacer net in the flow channel.

Today the spacer channel height has been increased from the original 24mil (0.60mm) to also include 30mil (0.76 mm), 50mil (1.27mm), 80mil (2.1mm), 100mil (2.54mm), and 130mil (3.30mm) spacers. It is also possible to design flow channels with a special spacer channel dimension to suit specific needs.

The dimensions of the most commonly used spirals are shown in Table 12 and the system is illustrated in Figures 50 and 51.

Table 13: Product specification for a range of RO/NF spiral wound elements.

RO/SW elements for solids concentration/water purification

Type	Rejection of NaCl %	Water flux 15.5 bar/25°C lmh	Maximum operating limits (continuous) bar	°C	Cleaning limits (short term) pH	°C
AMT ATFRO	99.5	N.S.	55	49	2-11	49
AMT ATFRO-pHt	99.5	N.S.	55	71	2-11	49
Desal-11 AF	99.5	33-45	41	50	2-11.5	50
Desal-3 SF	98.5	25-33	41	50	1-11.5	50
Dow FilmTec RO	>98.0	43-63	55	50	1-11.5	50
DSS Dairy ROpHt	N.S.	N.S.	42	50	1-12.5	60
DSS HR98PP	>96.0	N.S.	55	60	1-12.5	60
Koch TFC-RO-HR	99.0	40-53	69	50	1.8-11.2	50

NF/SW elements for demineralisation and low-MW fractionation

Type	Rejection of NaCl %	Water flux 6.9 bar/25°C lmh	Maximum operating limits (continuous) bar	°C	Cleaning limits (short term) pH	°C
AMT ASP10	10	N.S.	41	49	1-11.5	49
AMT ATF50	50	N.S.	55	46	2-10.5	49
Desal-5 DK	<50	33-44	41	50	1-11.5	50
Desal-5 DL	<40	45-60	41	50	1-11.5	50
Desal-5 DL DE	<40	45-60	41	80	1-11.5	50
Dow FilmTec NF	N.S.	26-43	55	50	1-11.5	50
Koch TFC-NF-SR1	30-50	N.S.	69	50	1.8-11.2	50

N.S.: Not specified

Table 14: Product specification for a range of UF and MF spiral wound and ceramic elements.

UF/SW elements for protein concentration

Type	Nominal MWCO dalton	Water flux 1 bar/25°C lmh	Maximum operating limits (continuous) Δ P (bar)	°C	Cleaning limits (short term) pH	°C
AMT AES10	5,000	N.S.	1.2	49	2-11.5	49
AMT AES30	10,000	N.S.	1.2	49	2-11.5	49
Desal PT	5,000	35-45	1.0	50	2-11.5	50
Desal PW	10,000	45-65	1.0	50	2-11.5	50
Desal PW-pHt	10,000	45-65	1.0	50/75	2-13	75
DSS UFPE	20,000	30-50	1.1	50	1-11.5	55
DSS UFpHt	20,000	30-45	1.2	70	1-13	70
Koch HFK-328	5,000	40-50	1.4	50	1.8-11.2	50
Koch HFK-131	10,000	55-65	1.4	50	1.8-11.2	50
Koch HFK-131 pHt	10,000	55-65	1.4	70	1.8-13	70
Synder HP99-MT	5,000	35-50	1.4	60	2-11	50
Synder HP99-ST	10,000	40-60	1.4	60	2-11	50
Synder HP99-MK	30,000	50-70	1.4	60	2-11	50

MF/SW and MF/ceramic elements for fractionation, clarification or bacteria removal

Type	Nominal Pore size nm/kd	Water flux 1 bar/25°C lmh	Maximum operating limits (continuous) Δ P (bar)	°C	Cleaning limits (short term) pH	°C
SW-membranes:						
AMT AF1000	1,000 nm	N.S.	1.3	49	2-11.5	49
AMT AF3U	3,000 nm	N.S.	1.3	49	2-11.5	49
Desal JX	300 nm	>140	1.0	50	1-11.5	<55
Synder HP99-FR	800 kd	90-100	1.4	60	2-11	50
Ceramic membranes:						
Orelis Kerasep BW	800 nm	>20,000	10	98	0-14	50/98
SCT Membralox Z	100 nm	2,000	10	120	0-14	50/80
SCT Membralox A	1400 nm	12,000	10	120	0-14	50/80
SCT Sterilox A	1400 nm	8,000	10	120	0-14	50/80

N.S.: Not specified

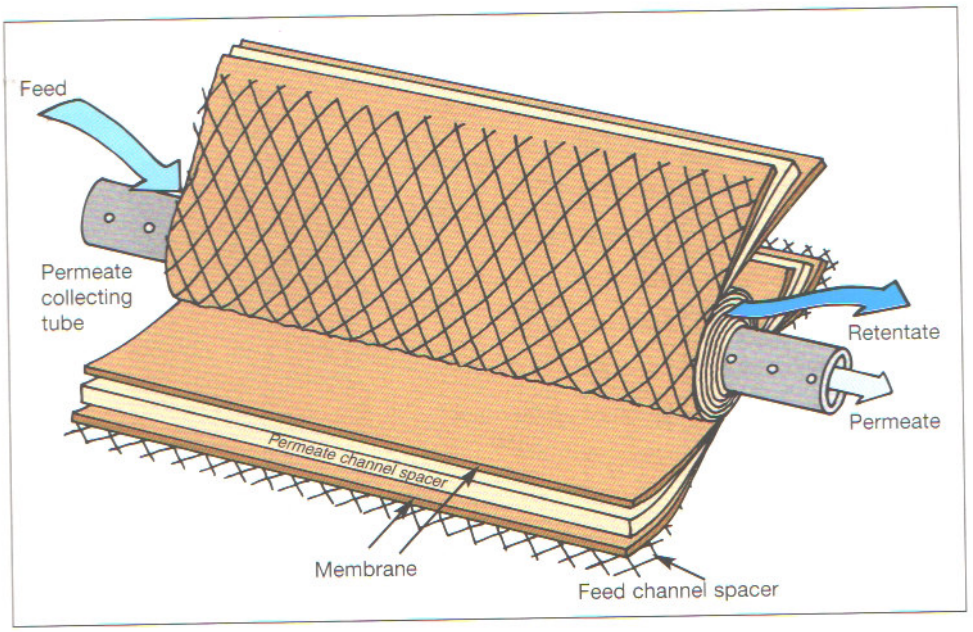


Figure 50: The spiral-wound element. The most remarkable and successful development, which today represents by far the largest volume of installed membrane systems.

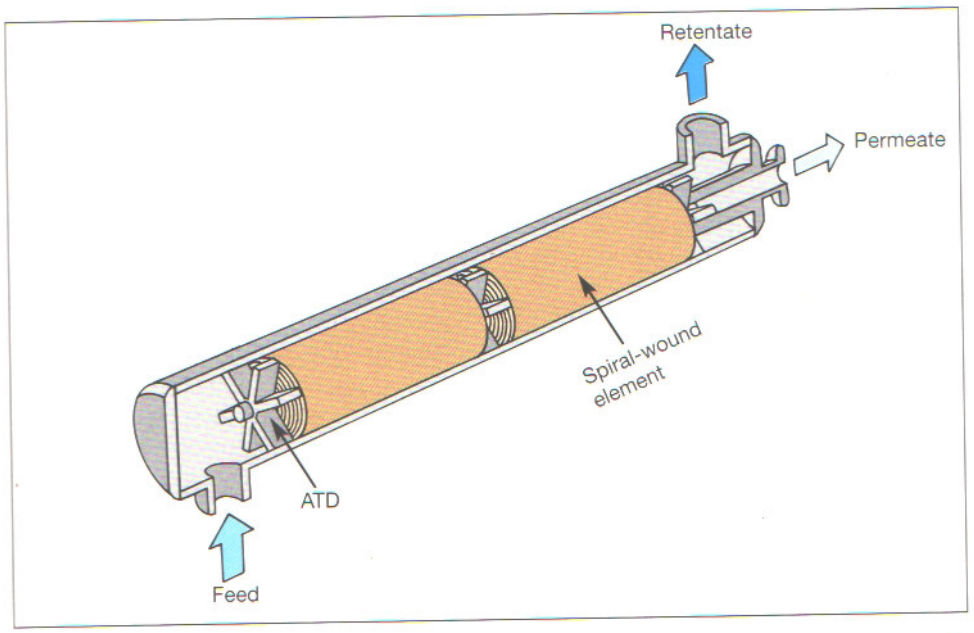


Figure 51: The spiral-wound module. Spiral-wound elements are fitted into appropriate pressure vessels. Depending on membrane type and a wide range of operating parameters, the number of elements in a pressure vessel may vary from one to six.

Table 13 and 14 gives an overview of a range of RO/NF, UF, and MF elements and some of their properties including the recommended temperature range.

Spiral-wound elements have today become the most commonly used membrane filtration elements of all, because of their unique design, low cost of manufacturing, low packing density, easy procedure for membrane exchange, and high level of versatility.

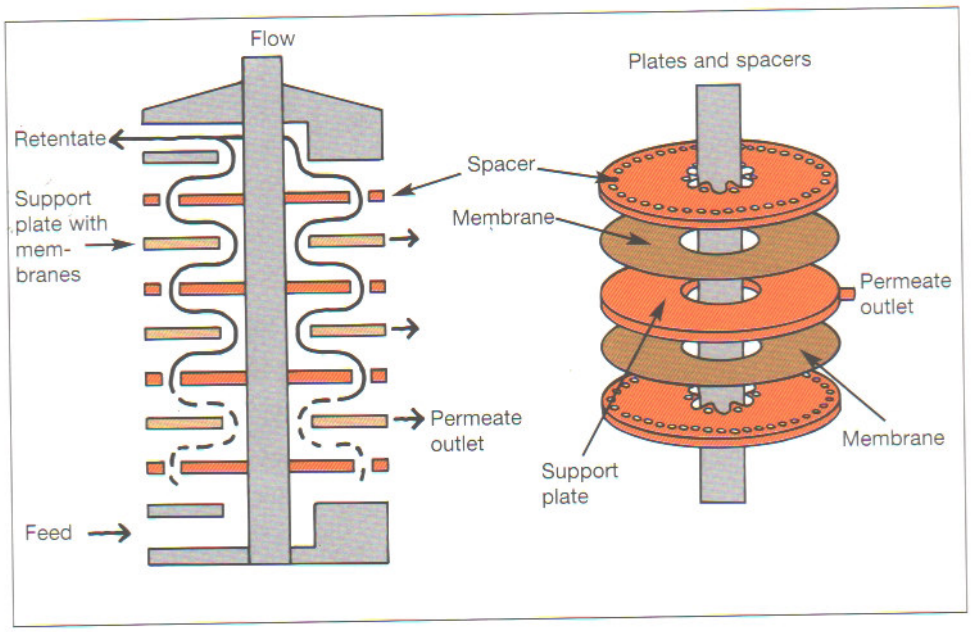


Figure 52: The plate-and-frame system for RO. Also one of the pioneering systems originally developed by Aerojet General. The DDS system illustrated in this figure soon became the preferred choice within plate-and-frame systems.

Plate-and-frame

The plate-and-frame system was originally designed by Aerojet General Corporation in California. It was designed for sea water desalination, and a number of trial installations were put into operation in the 1960s, but there were too many problems, and further development was not pursued.

In the early 1970s, DDS (the Danish Sugar Corporation) launched a new version of the plate-and-frame system, later followed by Rhône Poulenc in France. In more recent years, Millipore and Filtron in Massachusetts, and Sartorius in Germany have launched plate-and-frame casette systems for UF and MF.

The DDS System. The original DDS system is based on a series of circular flat sheet membranes mounted vertically. The membranes are placed on both sides of a porous, injection-moulded membrane support plate which serves as the collector of the permeate. The membrane support plate alternates with a plastic injection-moulded spacer plate. The membrane support plates and spacer plates are stacked around a central tie bolt, and the entire stack is hydraulically clamped together between two end flanges. The spacer plates have a groove in the circumference, which, in combination with the membrane and the membrane support paper, form an efficient seal enabling operation at up to 60 bar without any leakage. Each of the membrane support plates (0.1 m^2) is connected with a silicon tube to a common permeate collecting system. The spacer plates are designed so that channel systems are formed around the central tie bolt, which enables serial and parallel couplings internally in the modules.

Figure 52 illustrates the vertical DDS Module 30.

While the original system was designed for RO as well as UF, the next generation launched by DDS was designed especially for UF. The new horizontal design was launched in 1974. It consists of oval shaped membrane support plates (0.15 m^2) equipped with curved ribs and

one inlet and one outlet port for each plate. When clamped together by two flanges and two external tie bolts, the plates with membranes on both sides would shape a flow channel system (0.7 mm in height) which could easily be serial and parallel coupled in almost any way. The new system reduced manufacturing costs considerably because the spacer plate was omitted. The replacement of membranes was facilitated, and one membrane pair could easily be exchanged.

The design of the horizontal DDS Module 36 is illustrated in Figure 53.

A later improvement of Module 36 is designed especially for high viscosity products, and by varying the height of the flow channels, it is possible to obtain a more uniform flow velocity in all areas of the membrane plate. In this way, clogging of the product in the channels at an early stage during concentration can be avoided, and this design can operate at an extremely high viscosity.
The new Module 37, which can operate up to 20 bar, is shown in Figure 53.

An improved version of Module 37 (Module 39), which can contain up to 60 m^2 membrane area in one module, is the most recent development. Modules 37 and 39 are still used for high viscosity products such as quarg and cream cheese.

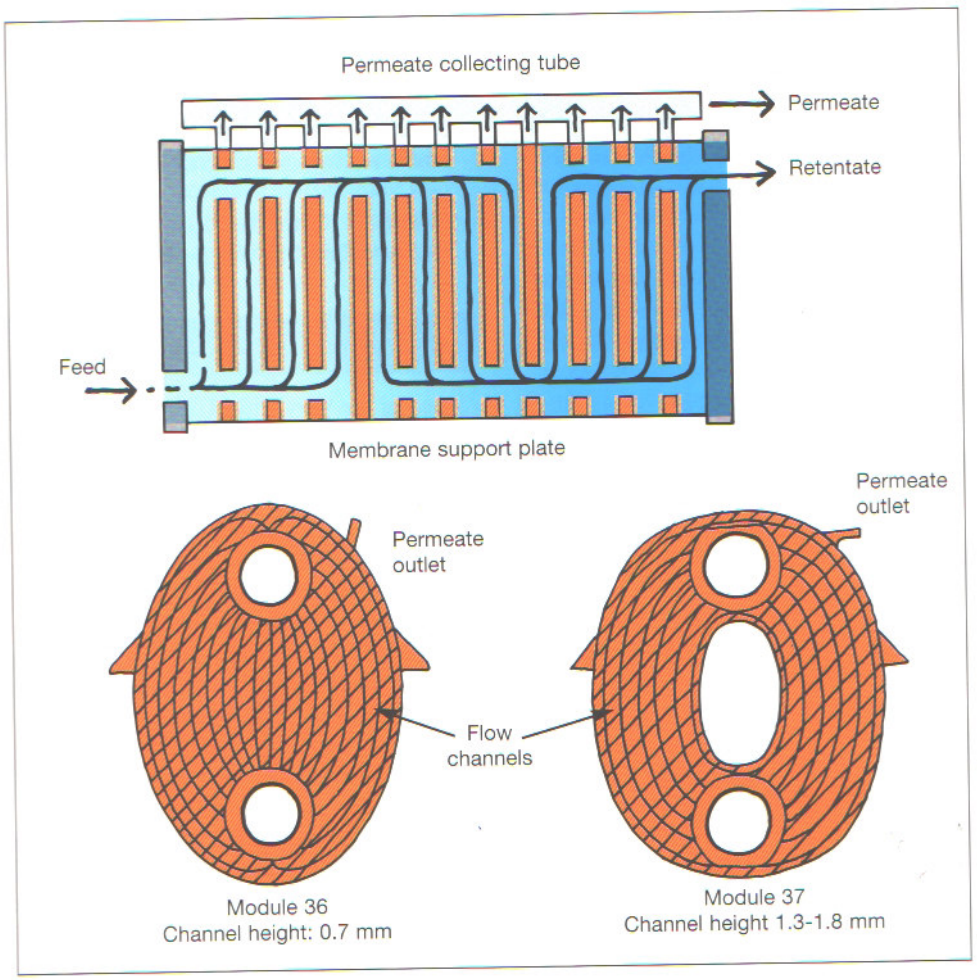


Figure 53: The plate-and-frame system for UF.
This system was developed by DDS and had a strong impact on the application of membrane systems in the dairy industry.

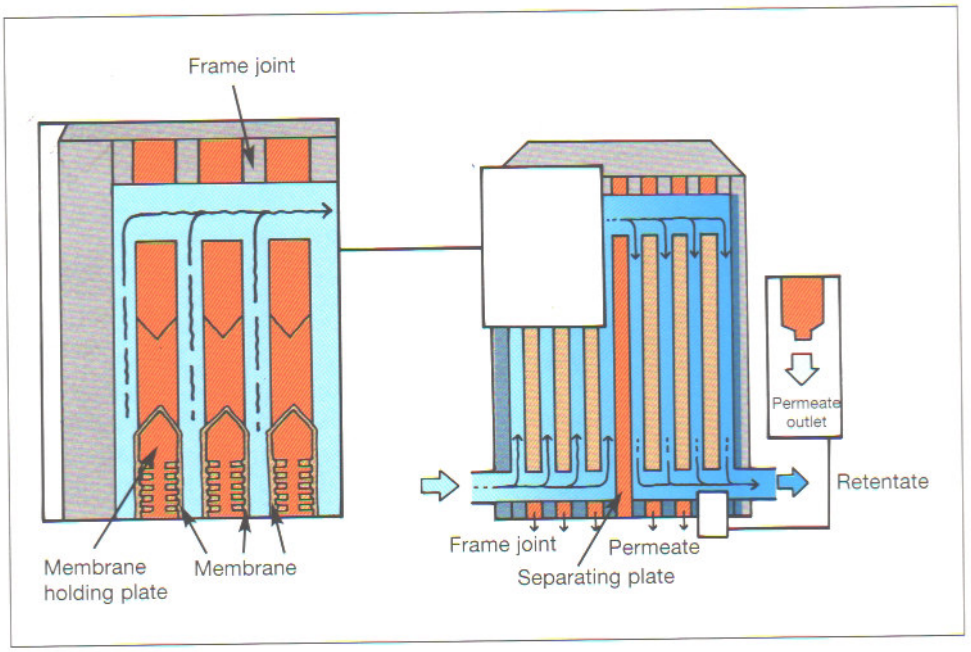


Figure 54: The rectangular plate-and-frame system. The PLEIADE system was developed by Rhône Poulenc and designed like a plate heat exchanger.

DDS membrane business was acquired by Dow Chemical in 1988. Part of the business was later sold to Danish Separation Systems.

The Rhône Poulenc System. The Rhône Poulenc system is based on rectangular plates with a 0.35 m^2 membrane area on each plate. The plates are assembled in a horizontal position in a type of plate heat exchanger frame.
The channel height is approximately 1.5 mm. Sealing rings and gaskets are used to tighten the module, and maximum operating pressure for the module is 6 bar.

Rhône Poulenc's membrane division acquired SFEC (Societé de Fabrication d'Elements Catalytiques) who held the licence from Union Carbide to manufacture the Carbosep ceramic system. The new conglomerate became known as Tech-Sep and launched the Kerasep ceramic membrane system, using aluminium oxide, titanium oxide and zirconium oxide as membrane and membrane support material. Today the membrane filtration group is part of Rhône Poulenc's environmental group, Orelis.

Figure 54 shows the PLEIADE UF system developed by Rhône Poulenc.

Parallel leaf

One of the very early UF module designs was launched by Dorr-Oliver in Connecticut. The Ioplate system consists of a rigid, rectangular plastic plate with the membrane heat-sealed on both sides. The membrane itself is cast on a fine support medium called a scrim. A drainage grid is placed between the scrim and the plate, allowing the permeate to flow with a minimum of resistance to a central collecting port. Several plates are stacked on top of each other, aligned by stubs on the periphery of the plates, and clamped together to form a cartridge. The permeate from the cartridges is collected in one common header. The original cartridge had a flow channel height of 2.5 mm, but in a later design the flow channel was reduced to 1.0 mm. The cartridges are

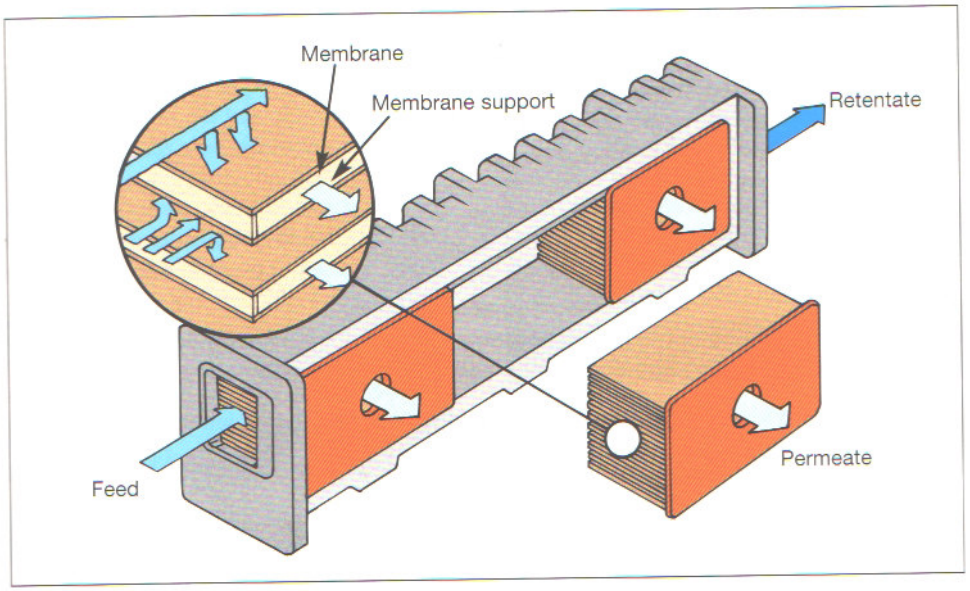


Figure 55: The parallel leaf system. One of the very early UF systems, successfully used for recovery of electro-phoretic paint in the auto-mobile industry.

placed in a stainless steel rectangular housing containing up to 12 cartridges. Each housing can contain 15.6 m^2 or 25.2 m^2 depending on the channel height. The system is designed for pressure up to 7 bar. The system has been successfully used for elctrophoretic paint recovery in the automobile industry.

Figure 55 illustrates the design of the Dorr-Oliver UF system.

Dynamic

Many attempts have been made to find new and better ways to diminish concentration polarisation and membrane fouling in order to improve operation, especially on products with high viscosity and a tendency to heavy fouling. One of these attempts has resulted in the Dynamic Membrane Filter (DMF) developed by Pall Corporation in the USA.

DMF is a system where fouling is minimised through creation of a shear force at the membrane surface which tends to lift contaminants away from the membrane surface. The shear is created in a gap between a rotating solid disc and the stationary membrane surface. This results in rotation of the bulk of the fluid as a nearly rigid disc, with significant shear in the boundary layer, formed on the membrane surface and on the rotating solid disc. The system is based on DMF element stacks of 0.25 m^2 shaped pieces of 180° element sectors. One module can contain 12 such elements, giving a total membrane area of 3 m^2. The diameter of the stack is 40 cm

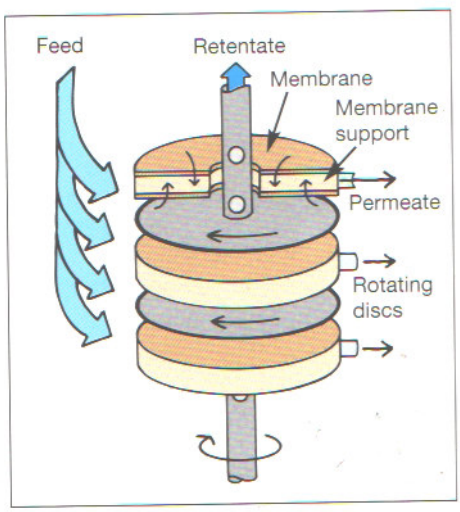


Figure 56: The dynamic system. A more recent development, where the velocity across the membrane is created by a rotating disc, operating at high speed. The system is developed by Pall.

and the maximum operating pressure is 3 bar.

The applications are very much related to the pharmaceutical sector e.g. for removal of cell debris from lysed cell cultures, as in the production of protein drugs. Figure 56 illustrates the operational principle of the DMF system.

Oscillating

Another way to reduce concentration polarisation and fouling is to oscillate the membrane. This concept was developed by the company New Logic in San Francisco, California.

The system is based on an oscillating disc filter stack vibrating at approximately 60 Hz around a vertical axis. Shear rates in the order of 100,000 to 150,000 sec^{-1} are generated at the membrane surface, and this focused energy is the essential feature that allows a long term stable flux. The membrane filter stack is designed for as much as 40 m^2 membrane area.

Two masses are connected by a torsion spring which is excited at its natural frequency. One of the masses is the membrane disc stack, and the other is defined as the seismic mass.

An AC motor, which is controlled by a variable frequency, solid state speed controller, is used to produce the excitation for the system. The motor spins an eccentric mass, mounted near the edge of the seismic mass. As the rotational speed of the eccentric mass is increased, the filter starts oscillating in response to the seismic mass with a 180° phase lag. The energy of the movement of the seismic mass is translated through the torsian spring to the membrane filter stack. The entire system rides on isolators to allow free movement.

Flow through the system occurs by pumping the feed fluid to the filter stack. The fluid permeates the membranes, and the solids in the process stream are retained on the feed side. The feed flow rate is controlled by a pump, and additional pumps or valves can be used to control flow rates or concentration fac-

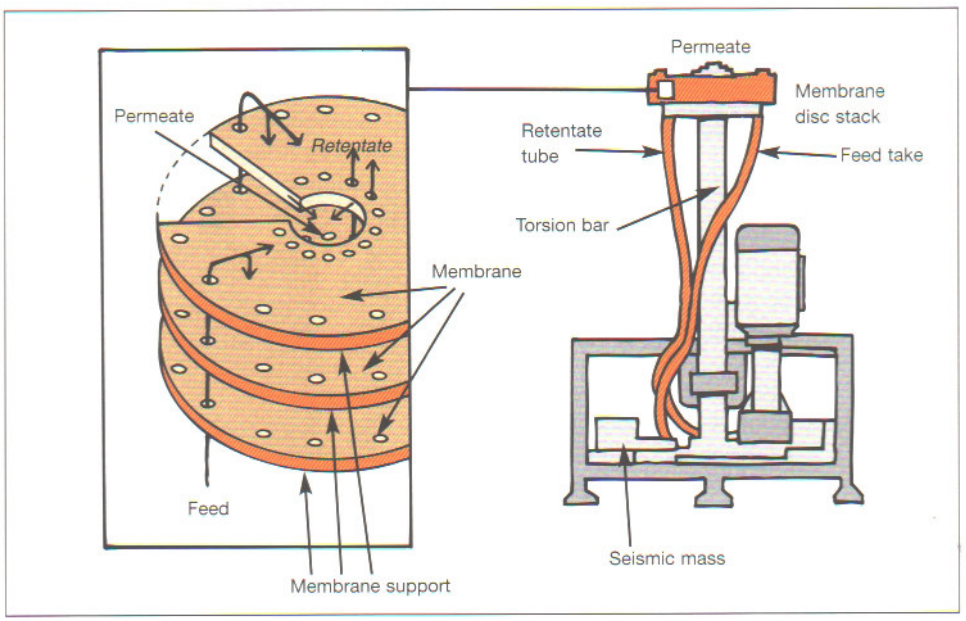


Figure 57: The oscillating system. This system is based on a concept where the entire membrane stack vibrates at a frequency of 60 Hz around its vertical axis. The vibrations reduce the concentration polarisation effects. The system was developed by New Logic.

tors. The system has been licensed to Pall Corporation and is marketed as the PallSep VMF Dynamic Filter System.

The applications are in the pharmaceutical industry, for biotechnology applications and in areas where conventional membrane filtration systems will have performance problems.

The oscillating system is illustrated in Figure 57.

Ceramic systems

Ceramic membranes have already been described. The technology for manufacturing ceramics is very different from that of organic membranes, and this also limits the configurations that can be used. So far the most common systems (Membralox, Kerasep, Atech) are manufactured as multi-channel systems, where the individual channels are from 2.5 mm to 15 mm in diameter. The length of the elements are usually in the range of 800-1200 mm.

The Membralox system, designed by SCT/Alcoa in France, is based on ceramic cartridges designed as hexagonal elements with up to 37 parallel channels. These elements are built into a stainless steel housing containing from 1 to 37 elements, giving a membrane area of up to 8.9 m^2 per housing. The housings are always placed in a vertical position, and both serial and parallel coupling is possible, depending on applications and volumes to be treated.

The Kerasep system designed by Tech Sep, a subsidiary of Rhône Poulenc in France, is similar in design. However, the cartridges are circular and it is possible to build as many as 99 elements into one housing, corresponding to 15.3 m^2 membrane area, with a channel diameter of 6.0 mm.

The Carbosep system, also designed by Tech Sep, is composed of individual carbon tubes, with a diameter of 6.0 mm and a length of 1,200 mm, built into a stainless steel housing with a maximum of 252 tubes, corresponding to a membrane area of 5.7 m^2.

Photo: APV

Figure 58: The ceramic system. A ceramic Membralox element in a stainless steel housing. Microfiltration is the most common application for the ceramic membrane systems.

The CeraMem ceramic filters were developed by Ceramem Corporation, Massachusetts, and based on the so-called honeycomb structure. Production modules are based on 6-inch diameter elements, 864 mm in length, with 2 or 4 mm channels containing 11.2 and 6.2 m^2 membrane area, respectively.

The ceramic systems have come a long way since they were launched in the early 1980s and are today the accepted system for high-performance MF.

Figure 58 shows the Membralox cartridge and illustrates how the membrane elements can be built into a stainless steel housing.

Other systems

In Japan, membrane filtration has attracted some of the major industrial companies. The greatest attention has been on waste water treatment and water desalination. To a large extent, the membrane systems developed are similar to the systems already described within spiral-wound (Toray), hollow fibre (Toyobo) and tubular (Nitto) systems. Teijin launched an asymmetric RO membrane, based on polybenzimidazole with excellent temperature and chemical stability.

The Japanese suppliers of membrane systems include the following:

- Asahi Glass Company Ltd
- Mitsubishi Heavy Industries Ltd
- Mitsubishi Kakoki Kaisha Ltd
- Mitsui Engineering & Shipbuilding Co. Ltd
- Nitto Electric Industrial Co. Ltd
- Sumitomo Heavy Industries Ltd
- Teijin Ltd
- Toray Industries Inc
- Toyo Soda Co. Ltd
- Toyobo Ltd

In Europe, a company like Hoechst, through its membrane division Celgard, has launched a membrane programme of both flat sheets and spiral-wound elements. Wafelin, today a part of Stork Friesland B.V. in Holland, launched a tubular system for UF, originally based on PVC tubes.

Table 15: A comparison of different membrane configurations.

	Back-flush capability	Requirement for pre-treatment	Level of compactness	Membrane replacement costs	Energy costs	Dead volume	Sensitivity to fouling	Handles high viscosity
Hollow fine fibres	yes	high	high	high	low	very small	high	no
Hollow fibre	yes	high	medium	high	low	small	high	no
Tubular	no	low	low	medium	high	large	medium	no/yes
Spiral-wound	no	high	medium	low	low	medium	medium	no
Plate-and-frame	no	medium	low	medium/ low	medium	medium	low	yes
Parallel leaf	no	low	low	high	high	large	low	no
Dynamic	no	medium	low	high	low	medium	low	yes
Oscillating	no	medium	low	high	low	medium	low	yes
Ceramics	yes	medium/high	medium	very high	high	medium	medium	yes

The membrane systems discussed above are the most relevant at present. However, many other membrane systems are available or in the development phase.

Comparison of systems

In this chapter, the most common membrane systems have been described. Each system has benefits and drawbacks, very much depending on the specific application. The various systems have been developed and designed for specific applications, and consequently it is quite difficult to make a general, meaningful comparison. There are, however, some features like dead volume, energy consumption, requirement for pre-treatment, ease of membrane exchange etc., which it may be useful to compare.

Sensitivity to fouling	Handles high viscosity
high	no
high	no
medium	no/yes
medium	no
low	yes
low	no
low	yes
low	yes
medium	yes

9 Ion exchange systems

The conventional way of using ion exchange resins is to pack them into columns ranging from a few 100 millilitres to more than 1.000 litres for industrial scale columns. The columns are specially designed vessels, equipped with inlet and outlet for product, regeneration liquid, backflushing liquid, and rinse water.

Since the regeneration is based on strong acids (sulphuric acid 1.5-5.0% w/v) and strong sodium hydroxide (5.0% w/v), it is essential always to use the right construction materials. A common way to construct the columns is to use rubber-lined mild steel to combat any corrosion problems.

Since ion exchange resins tend to swell - this is especially true for anion exchange resins - it is also common to design the columns in a slightly conical form, allowing for resin expansion during the transition from the free base form to the salt form.

Counter-current flow is sometimes used for regeneration of ion exchangers. Such systems reduce the consumption of regeneration chemicals by as much as 30-40%, but at the expense of a more complicated design.

Mixed-bed ion exchangers are columns filled with a mixture of strong acid and strong base ion exchange resins, and this represents a very powerful unit for demineralisation of water to the highest purity. The resins comprise an intimately mixed mass of the two resins and can be regarded as an infinite number of micro-demineralising pairs of columns. Cation and anion exchange occur simultaneously, yielding a water with very high purity in one stage. Under such ideal conditions

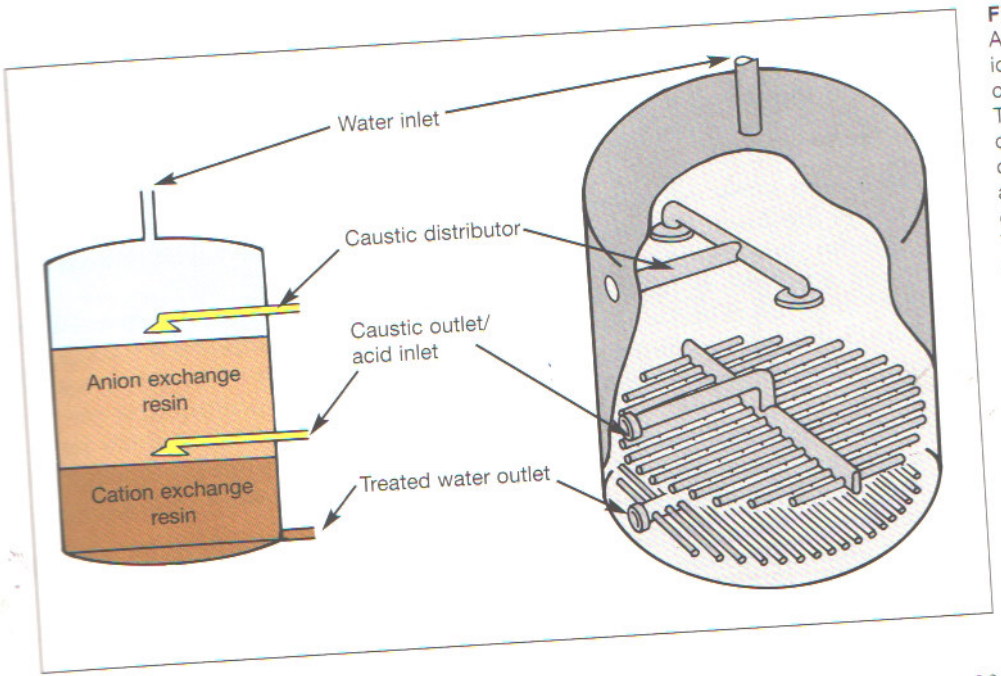


Figure 59: A mixed-bed ion exchange column. The column contains both cation and anion exchange resins. The column is able to remove all salts in water in one stage and reduce the conductivity to 0.04 µS/cm.

it is possible to produce water with a conductivity of 0.04 µS/cm with as little as 0.002 ppm silica.

The regeneration of mixed-bed units is complicated, however, and involves a prior separation of the two resins by elutriation followed by individual regeneration. The resins are then rinsed and remixed.

The regeneration principle of a mixed bed ion exchanger is shown in Figure 59.

10 Chromatographic systems

Chromatographic systems are in many ways similar to ion exchange systems. The variety in resin types and the range of applications however, are far beyond what is known for ion exchange, and this has created a need for more sophisticated systems.

The need for large scale processes for whey separation led to the development of the stirred tank batch process. Thus, the search for a less complicated scale-up procedure and a better utilisation of the resins, led to the development of the radial flow chromatography columns. And the search for better resin utilisation and a continuous process led to the development of a continuous system based on a carousel concept.

Axial flow column system

The axial flow system is still the most common system used for both ion exchange and chromatography, and the designs of the columns are similar to the ones described in Chapter 9. However, when chromatography is used for high molecular weight separation, such a system presents certain disadvantages:

- *Blockage of column*. To achieve fast kinetics of adsorption and desorption, the resin particles must be small. The very small particles function as a filter which can easily block when solutions of large molecular weight products are treated

- *Pressure drop*. The small particles cause the pressure drop to increase as columns are scaled up by increasing the height of the columns. Increasing pressure drop contributes to reduction of the resin life time, especially for the more fragile type of resins

- *Channel formation*. As the column height increases, there is an increasing risk of formation of channels through the resin bed, through which the feed liquid will tend to pass, and this will contribute to poor utilisation of the resin.

To summarise: this means that axial flow columns are restricted in size, and that the types of resins which can be utilised are limited.

Stirred tank system

In the stirred tank system for whey protein fractionation, the liquid to be treated is slurried with the chromatographic resin until adsorption has occurred. The de-proteinised solution is then removed, and the resin is washed with water prior to desorption of the proteins with acid, alkali and/or mineral salts.

Compared to the column system, the disadvantage of the stirred tank system is that not all the proteins are removed, due to the equilibrium conditions. This problem can be solved in part by re-feeding the de-proteinised solution to the resin before the next batch of whey is treated.

The stirred tank system allows the use of larger resin particles, since the contact time between resin and liquid can be increased. This facilitates the removal of the process solution and makes the process less sensitive to fat and suspended solids.

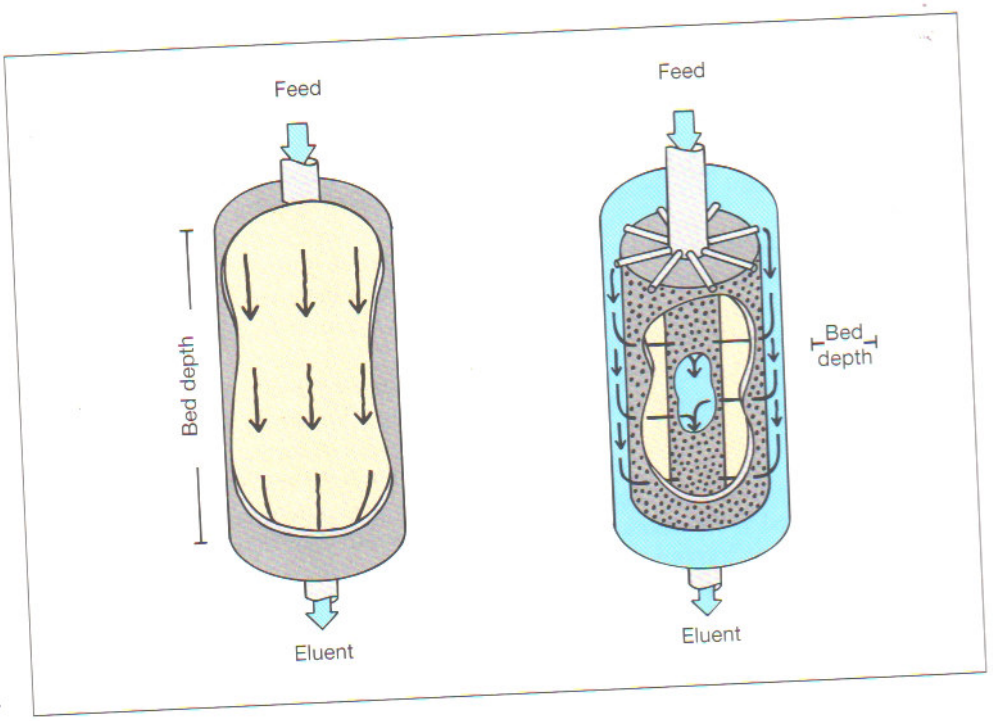


Figure 60: The radial flow chromatographic system. In the radial flow column, the liquid flows along the radius, reducing the flow path considerably compared with conventional axial flow columns. This reduces the pressure drop in the column, the strain on the resin, and improves the overall performance of the system.

Also, fewer overall changes in pH are required during the complete adsorption/desorption cycle, reducing the risk of protein denaturation, and improving the final product quality.

The stirred tank system allows the use of the regenerated GibcoCel™ resin (see Chapter 5) which has proven to be an ideal resin for the production of isolated whey proteins. The process is described in more detail in the section on dairy applications in Chapter 14.

Radial flow column system

Chromatographic columns may range in size from less than one millilitre to more than 1,000 litres.

As applications have developed, the problems of scaling up to large capacities have become more apparent. Basically, liquid chromatography is a relatively slow process. Previous attempts to accelerate the performance have resulted in reduced separation performance and capacity. As axial flow chromatography processes are increased in scale from laboratory quantities to commercial production quantities, productivity and efficiency typically decrease. Time consuming trial and error steps are used to re-optimise the process several times during scale-up, to improve productivity and efficiency. The speed in conventional chromatography is limited by the column's cross-sectional area, longer bed depth, and resulting higher pressure. Conventional liquid chromatography purification on a laboratory scale generally requires several hours to complete and, in commercial scale applications, may require up to several days.

The radial flow chromatography technology was developed by Sepragen, a Californian based corporation, to solve some of these problems.

In radial flow chromatography, the flow is perpendicular rather than parallel to the axis of the column. The liquid mix-

ture containing the target molecules flows horizontally from the outer sidewalls of the column through the separation media towards an outflow channel in the centre of the column.

This system permits the production volume to be increased without any significant impairment to the quality of purification and without the need for high hydrostatic pressures. It results in greater quantities of purified product produced more efficiently than with the traditional chromatography processes, and the resins are utilised more efficiently. While still significant at lower volumes, the importance of these advantages increases as the volume of the compounds to be processed increases to thousands of litres and tonnes, and as the per unit cost of processing grows relative to the selling price of the products produced.

Figure 60 compares radial flow chromatography with conventional axial flow columns.

The expanded-bed system

Expanded-bed adsorption or stabilised fluid bed chromatography is a new concept in chromatographic separation. The basic idea is to fluidise the chromatographic beads by an upward liquid flow and thereby avoid the problems associated with traditionally packed bed chromatography, e.g. increased back-pressure due to clogging of the bed and the distribution plate by impurities in the feed stock.

In a fixed bed, particulate impurities accumulate if crude feed stock is applied because the chromatographic bed functions as a depth filter. In an expanded bed, the chromatographic beads are separated and particulate impurities can pass through the bed without accumulating. In order to obtain an efficient expanded-bed adsorption system, it is important that the chromatographic beads stay relatively fixed in their vertical position during fluidisation. This is achieved by using beads with specific size and density range and by ensuring plug flow through the expanded bed.

UpFront Chromatography - a Danish company based in Copenhagen - has developed a range of Fastline™ columns based on the expanded-bed technology. After introduction at the bottom of the column, the feed is distributed evenly over the cross section of the column by a special stirring device which secures an equal distribution of the upward flow. Sample application, washing and elution are all performed in the expanded bed mode, which assures fast and simple purification of the feed.

The resins, or matrices, developed for the expanded-bed columns can be tailored both in respect of density, density distribution and ligand chemistry.

11 Continuous column systems

Both ion exchange and liquid chromatography are inherently batch processes. As in any other area of process technology, attempts are made to find ways to convert the batch process to a continuous process.

In the early 1990s Advanced Separation Technologies Inc., a company based in Florida, introduced the ionic separator ISEP® as a continuous ion exchange unit.

An ISEP® contactor includes a carousel of 30 short-fixed bed cells which rotate continuously at a specific rate. Each cell contains adsorbent media, in the form of an ion exchange resin, activated carbon, molecular sieves, etc., contained within two retention screens. The cells are equipped with upper and lower nozzles in an upper and lower rotating distributor head, which is driven by the same motor used to rotate the carousel. The inlet and outlet rotating distributor head is matched to a stationary distributor head, containing two sets of 20 equally distributed nozzles or fixed ports. The flow into or out of these fixed ports is constant and uninterrupted while the unit is in operation. The speed of rotation of the carousel is in the range of 0.1 to 1.4 revolutions per hour.

During a 360° carousel rotation, each resin cell will be subjected to an entire sorption cycle, which usually consists of adsorption, rinse, regeneration or elution, backwash, and one or two rinsing steps. At any point in time, either one or two resin cells receive flow through a partic-

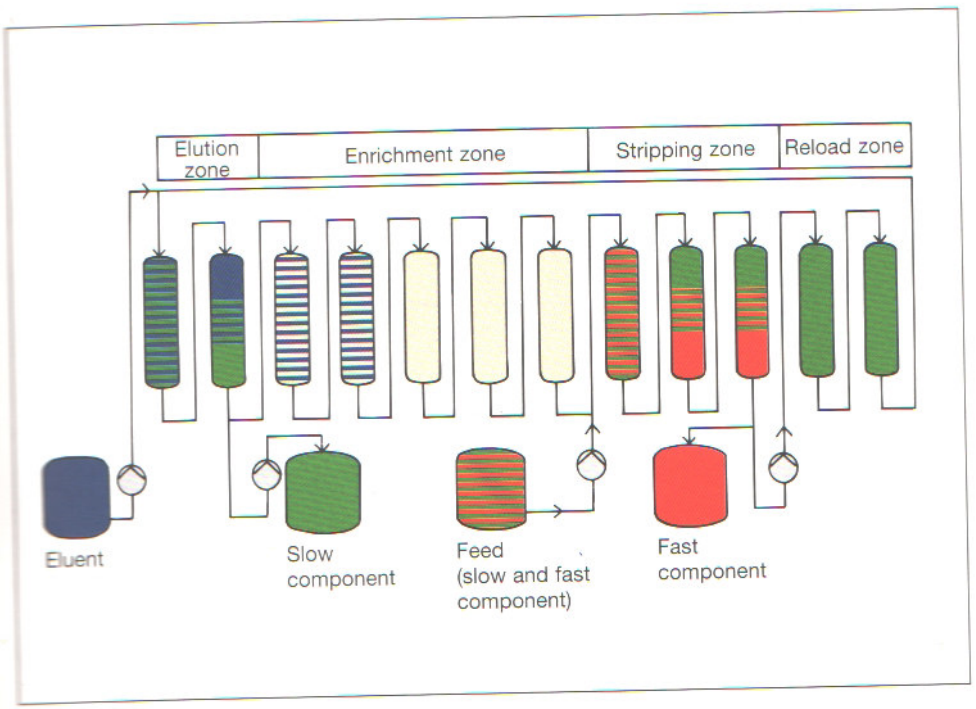


Figure 61: Continuous counter-current chromatography system. A number of columns rotate in a carousel at a specific rate. During the rotation, the columns are connected through stationary distributor heads (fixed ports) through which liquid for the entire sorption cycle is provided.

ular fixed port. As a cell passes from under one port, the flow to it is stopped momentarily until it passes under another port, thereby ensuring that a resin cell receives flow from only one port at a time. None of the resin sits idle in the cell in either its exhausted or regenerated state during the adsorption cycle, resulting in a much lower resin inventory than with conventional ion exchange or chromatography systems.

A more recent development, CSEP®, are using continuous chromatography separation processes.

The major difference between the batch column chromatographic processes and the continuous co-current chromatography is that the batch column fractions are collected in a time sequence, whereas the continuous column fractions are produced continuously at a relatively constant composition.

Figure 61 illustrates the principle design of the continuous system for a 12-column chromatography unit.

The continuous systems are used extensively in the production of corn syrup and lysine, and the food processing and pharmaceutical industries are showing a growing interest in this technology as well.

12 Process design

The previous chapters have reviewed the basic processes, the membranes and resins, the different systems and configurations, and the mechanisms for concentration polarisation and fouling. The next step is to design systems which can handle specific volumes of products on an industrial scale, at the lowest possible cost, reaching a defined specification of a final product.

In order to do so, plants must be carefully designed. The technologies referred to so far are all modular in nature, but this chapter will consider how the modular concept can be converted into plant designs which can achieve the objective stated above.

Modes of operation

There are a number of different approaches to the design and layout of membrane plants. Is batch or continuous operation required? If continuous, should it be single-pass plug-flow, or multi-stage with recycling? And in the case of multi-stage, how many stages are needed, and must they all be of the same size and design?

This chapter will define some of the more basic principles, followed by examples of plant design and information on automation and cleaning.

Batch

This is the most simple way to operate a membrane system. The concept is illustrated in Figure 62. The recycling loop will usually include a heat exchanger, which can remove the heat generated from the pump. The concentrate is recycled to the feed tank until the final concentration is reached.

This is the fastest way to concentrate a given amount of feed. It requires the minimum membrane area to do the job, and it can operate with a minimum of automation. This concept is frequently used for lab units and small pilot plants. The retention time in the plant can become quite long, which limits operating temperatures somewhat.

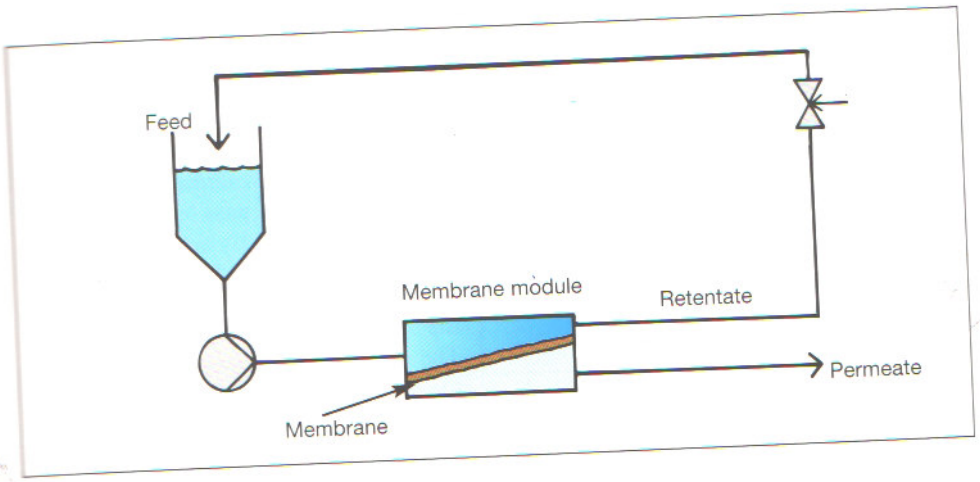


Figure 62: Batch system. The most simple way to operate a membrane system.

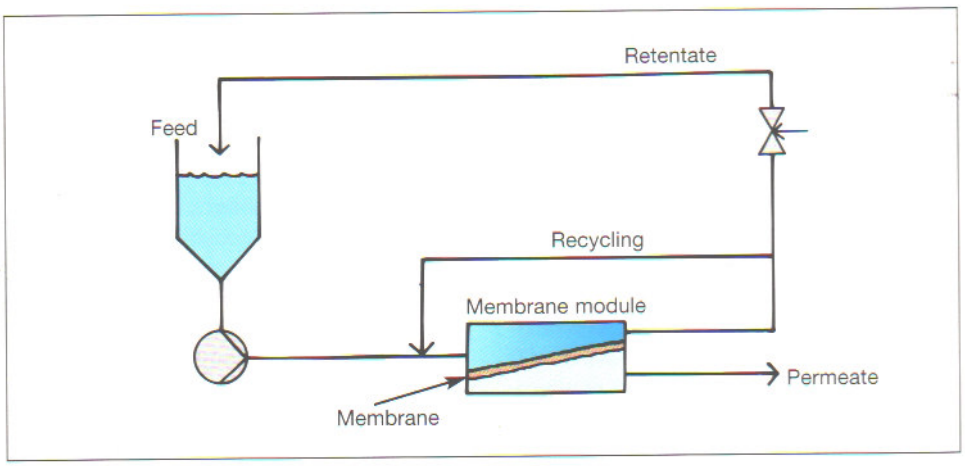


Figure 63: Batch system with recycling. A modification of the batch system, requiring less energy.

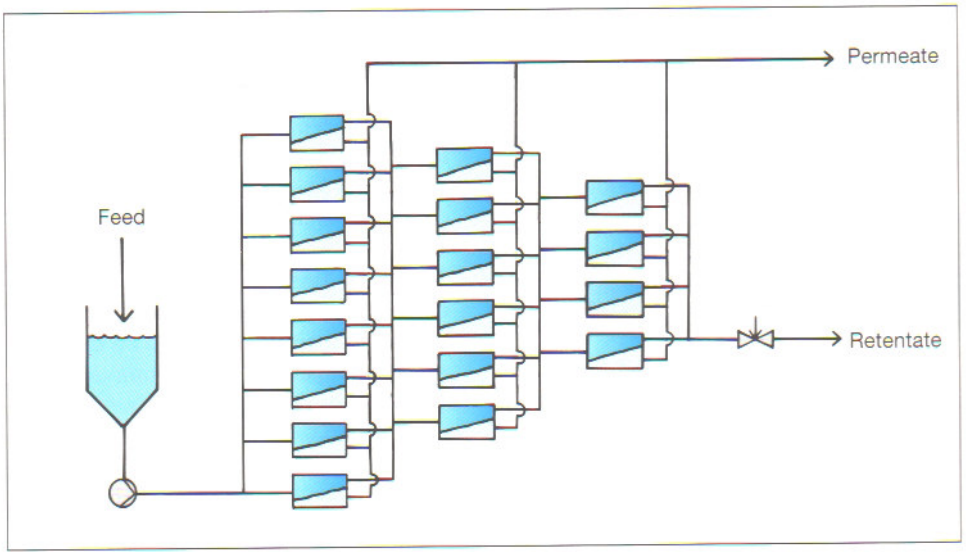


Figure 64: Continuous single-pass system. The most simple and inexpensive way to operate a continuous system. The system is used mainly for low level RO concentration of feed solutions with very constant and stable properties.

Figure 63 illustrates a variety of the batch system called 'batch with recycling'. This system requires less energy and more membrane area to do the same job. If fresh product is fed to the recycling tank at the same rate as permeate is removed, the system can operate continuously. This is also known as the 'semi-batch system'. Since the module in this case will operate at the high outlet concentration all the time, the capacity may be considerably reduced.

Continuous single-pass

In the single-pass continuous system, the feed solution passes only once through the modules, i.e. there is no recycling. Consequently, the volume of feed decreases with the pass length, and this is compensated for by arranging the modules in a tapered design as shown in Figure 64. This is also called the Christmas tree design or the plug flow system. The reduction in membrane area through the system is made in such a way that the flow velocity across the membranes is kept at a constant level, or even

increased to counteract the growing tendency to concentration polarisation, due to the increasing concentration of solutes. The volume reduction factor, or the degree of concentration, defined as the ratio between feed and concentrate, is determined primarily by the module arrangement.

The advantages of the single-pass system are low energy consumption, short residence time, optimum flux rate and a simple design. However, the single-pass system requires that the product is uniform from day to day, that all operating parameters are pre-set, and that the degree of concentration is relatively low. The system is only used for RO systems with a very uniform feed and a low level of concentration such as systems for desalination of sea water, where the feed has been subjected to careful pre-treatment.

Continuous recycling

In this system, the feed is pumped into a common feed line for a number of stages, where each stage is equipped with its own recycling pump to optimise the flow conditions across the membranes in each part of the plant. The system is illustrated in Figure 65.

This design enables adjustment of flow and pressure in each individual stage. The residence time, the dead-volume, and the tank capacity requirements are much lower than for batch operation. Furthermore, such systems can be operated in a sanitary manner and efficiently cleaned and sanitised when required.

Normally, such systems are operated on a 24 hour-basis, with a 2-4 hour break for cleaning. The average flux rate is reduced in comparison with a batch operation at the same temperature. This is compensated for by increasing the number of stages. More stages mean higher investment and, consequently, an optimum design can be determined. Due to the low residence time, the lower capacity may be compensated for by increasing the operating temperature.

The system can be fully-automated and equipped with control functions and alarm functions common to the industry environment in question.

In order to determine the number of stages in a continuous plant, it is necessary to know the flux curve as a function of the degree of concentration. This is illustrated in Figure 66, which shows the

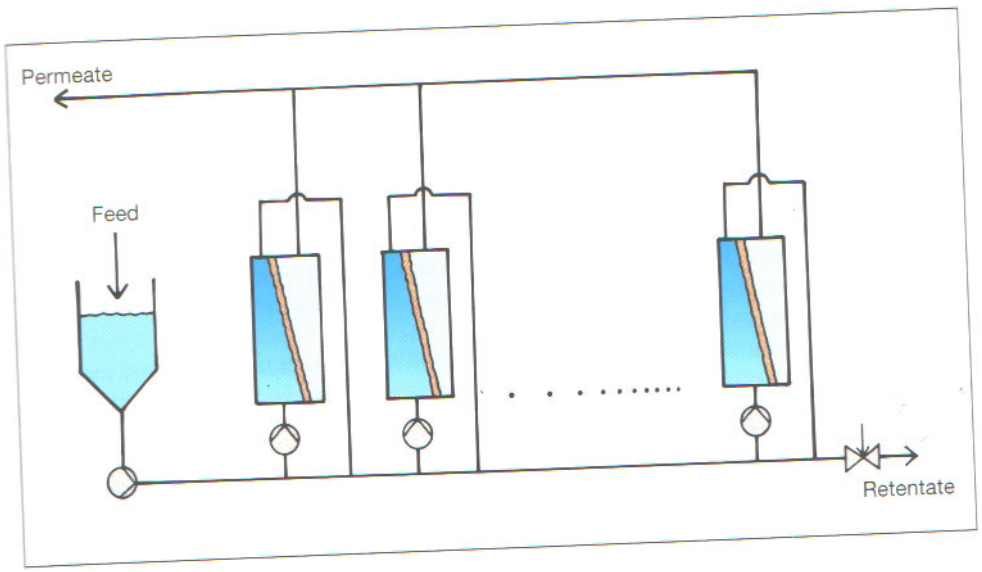


Figure 65: Continuous system with recycling. The most common way to operate a continuous membrane filtration system. A variable number of stages may be applied.

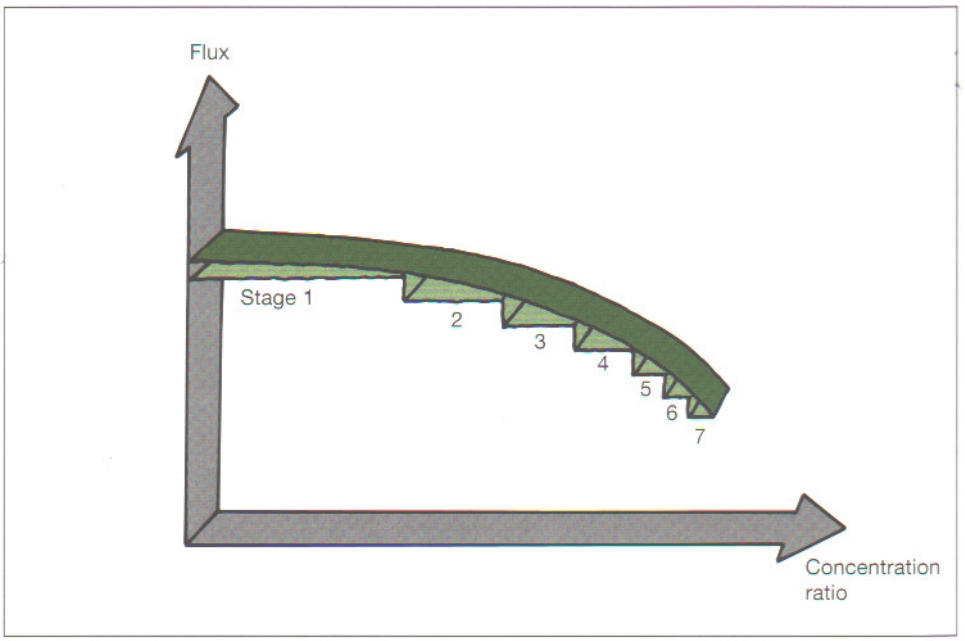


Figure 66: Based on the flux curve as a function of concentration ratio, it is possible to estimate the number of stages needed in a continuous plant.

flux curve for a plant with seven stages. As already mentioned, a low number of stages means more membrane area. For various products it is possible - by means of mathematical modelling - to make dimensioning programmes, which calculate the optimum number of stages required to reach a defined product, based on an analysis of the composition of the feed, and determination of operating parameters, such as pressure, flow rate and temperature. Furthermore, each individual stage can be optimised for the concentration reached in exactly this stage.

The continuous recycling system is almost always used for MF and UF operations, and in most cases also for NF and RO systems, and it is recommended always to consider this system since it is well-proven, and provides the safety and flexibility in operation which is so important in successful utilisation of membrane filtration technology.

Diafiltration

Diafiltration is a process in which water is added to the product during membrane filtration. The purpose is to remove solutes which are able to pass the membrane. The percentage of desired solutes in the total dissolved solids is defined as purity. The reason for using diafiltration is that it makes it possible to obtain a purity, which cannot be obtained by the conventional membrane filtration process.

In the production of whey protein concentrate, diafiltration is used to remove lactose and salts in order to reach a high purity for the whey proteins. In concentrating of enzymes, diafiltration may be used to remove undesired salts, amino acids and other low molecular weight compounds in order to increase the purity of the final product.

Diafiltration requires additional membrane area to remove the added water. The amount of water needed to obtain a specific purity can be calculated and optimised when the permeability of the solutes to be removed is known. In continuous plants, the addition of water is

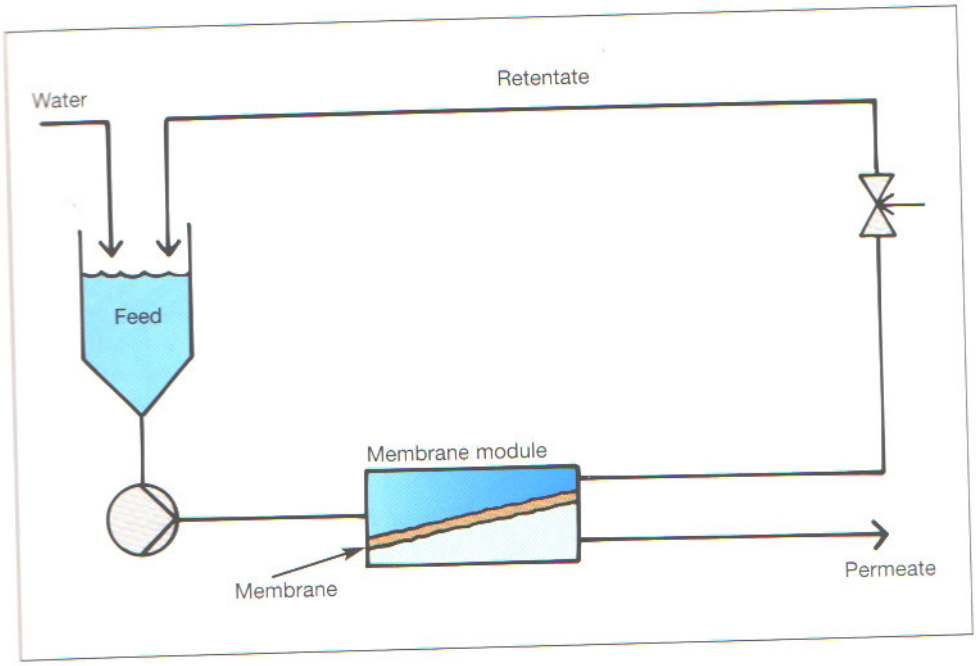


Figure 67: Diafiltration in a batch system. In diafiltration, water is added to the feed solution in order to remove additional solutes with the permeate. In the batch system, the water is added in the recycling tank.

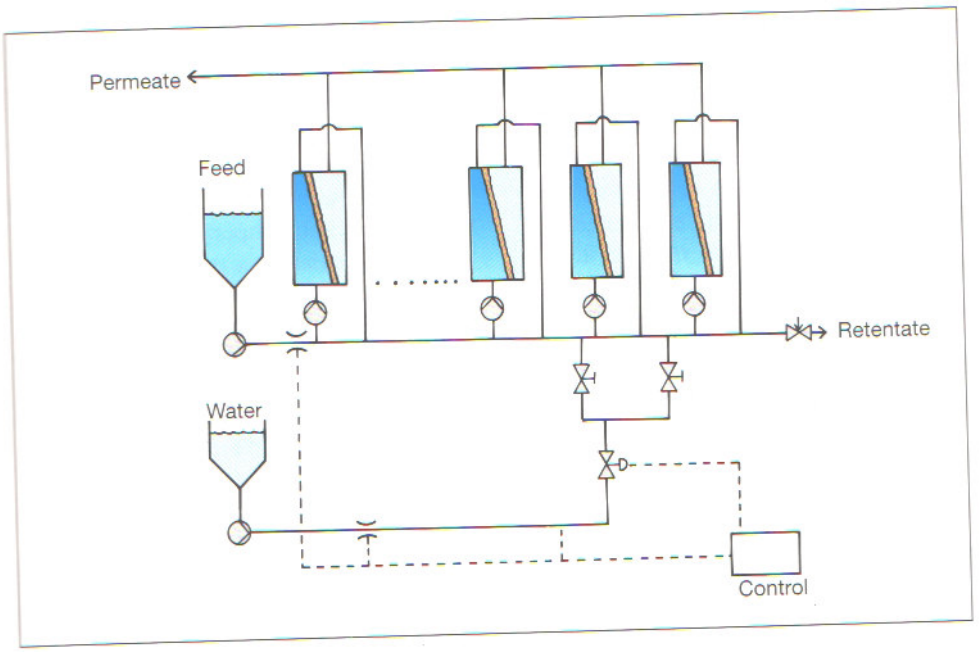


Figure 68: Diafiltration in a continuous system with recycling. The diafiltration water is added at a number of pre-calculated stages and automatically regulated.

normally split up in several stages in order to utilise the diafiltration water most efficiently. Figures 67 and 68 illustrate the principles of diafiltration for a batch system and for a continuous system with recycling.

System design

The design and engineering of membrane filtration systems, electrodialysis systems, ion exchange systems and chro-

matographic systems is the key to successful industrial and commercial utilisation of these technologies. The design and engineering expertise available today stems from many years' experience.

For a long time, membrane filtration was surrounded by an aura of uncertainty in respect of full-scale operation, but today the engineering is sound and well-proven on a level with other unit operations in industry.

In system design and engineering, a distinction is made between sanitary and industrial designs. In sanitary designs, the recommendation laid out by the EHEDG group (European Hygienic Equipment Design Group) should be followed just as the American USDA/3A must be carefully considered. Certain industries, like pharmaceutical and health care, may have specific requirements, e.g. to surface finish.

In this section, a brief review is given of the most typical design principles for the most important systems.

RO/NF systems

The design is based on a continuous recycling system. From a feed balance tank, the product is fed into the feed line. The feed pumps are usually of the multi-stage centrifugal feed pump type, but in some cases positive displacement pumps may be used. From the common feed line, a recycling pump (booster pump) circulates the feed through the modules installed in the first stage. The concentrate from the outlet of the membrane modules is fed back to the feed line. The pressure loss through the modules determines the flow rate across the membranes and is determined by proper sizing of the booster pump.

The second stage is basically designed like the first stage but as the feed passes down through the system and the concentration of solutes increases, the viscosity may increase, requiring a higher pressure drop to maintain the correct flow conditions across the membranes. Sometimes, the type of module or the module configuration may be changed in order to maintain optimum process parameters throughout the system.

To be able to control the operating temperature, a tubular cooler is usually installed in each recycling loop. After the last loop, the concentrate has reached its final concentration, and is transferred for further processing.

The permeate is collected from the elements in each loop in a common permeate collection system and transferred for further processing. It is common to install a flowmeter at the permeate outlet of each loop in order to control the performance both during operation and during cleaning-in-place (CIP) of the system.

During CIP, both permeate and concentrate are fed back to the balance tank for recycling of CIP chemicals and the cooler may be used to heat the cleaning liquid to the required temperature.

Each loop is built to a standard design, which depends on the type of module used. For spiral-wound modules, the loop consists of a number of parallel pressure vessels connected to a common manifold at the outlet and inlet.

The pressure vessels are standardised for a certain element diameter and length. The most commonly used standards are pressure vessels for 4-inch, 6-inch or 8-inch diameter elements, each containing from one to six elements in series.

If diafiltration is a part of the system, diafiltration water is injected from a separate tank into the feed line at the appropriate stages in the system as illustrated in Figure 68.

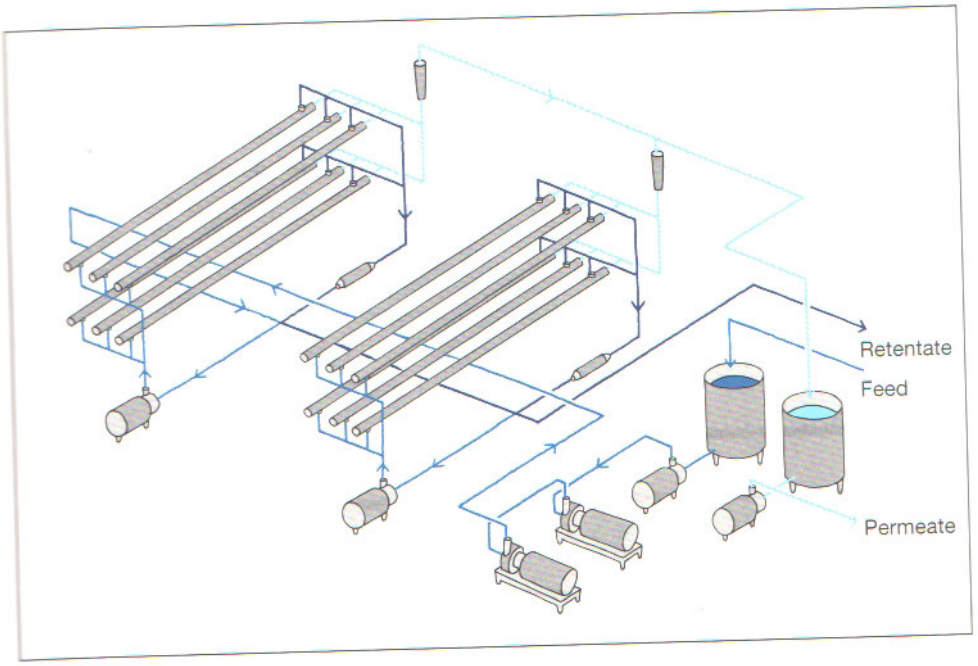


Figure 69: Layout of an RO plant with 4-inch spiral-wound elements. The various parts of the system are standardised, reducing the need for design and engineering of each system.

The system is equipped with the necessary transmitters, instruments and sensors in order to automate the system. This will be described in more detail in the section on automation at the end of this chapter.

RO and NF systems are basically designed in the same way, except that the membranes are of different specifications, and that NF plants will normally operate at a lower operating pressure than RO plants. Figure 69 shows the layout of a continuous RO plant with recycling and equipped with 4-inch spiral-wound elements.

UF systems

UF plants are normally based on the continuous system with recycling. In many ways, the design is similar to the system described for RO/NF systems, but with some important differences.

Figure 70 illustrates a two-stage UF system based on 6-inch spiral-wound elements. In this case, the balance tank is of a double construction with two compartments, one for feed entering the plant, and another for permeate leaving the plant. An overflow is mounted between the two halves of the balance tank, which makes it possible to return some of the permeate to the plant. This facility is used at the start-up of the plant when the capacity of the UF plant exceeds the capacity of a possible pre-treatment plant. At the end of a production run, this facility is used to empty the plant in the sense that the permeate 'pushes' the product out of the plant. The overflow also enables recycling across the entire UF plant during CIP, and in case of insufficient supply of product to the plant.

After the balance tank, a feed pump and a valve for control of the feed pressure are mounted. This is to secure a constant inlet pressure to the system, which is important for the supply of feed to the individual loops. In order to protect the membranes, a metal screen filter for removal of impurities left in the product is mounted after the feed pump.

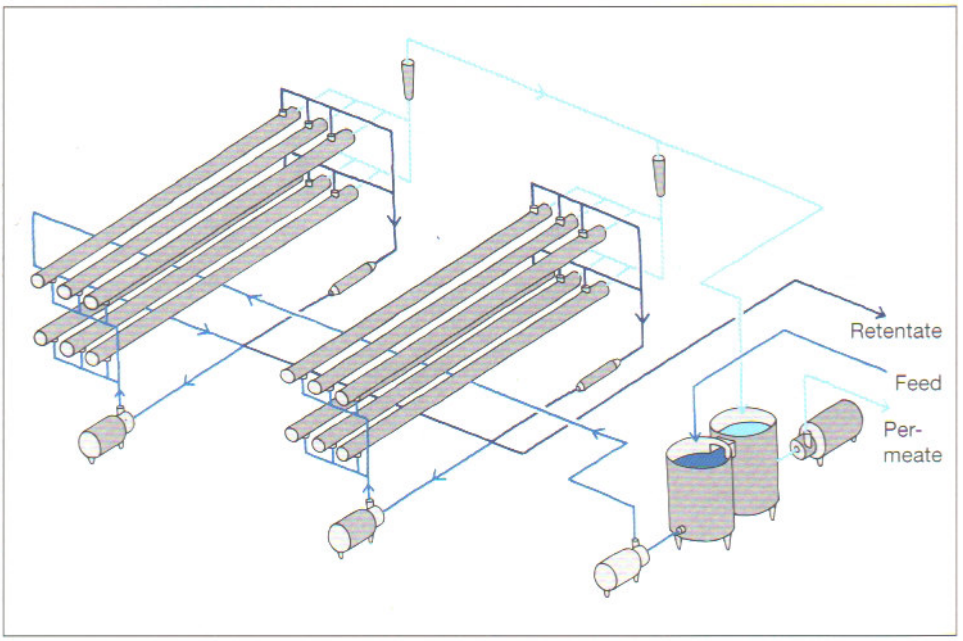


Figure 70: Layout of a 6-inch UF plant with spiral-wound elements.

The individual loops are in principle designed as for the RO/NF system, but with some important differences. UF concentrates macro-molecules, and the viscosity may increase considerably during the process. In order to secure optimum flow conditions throughout the plant, the configurations of the last loops are altered with a smaller number of sections (plate-and-frame) or membrane elements with a higher product spacer (spiral-wound) and fewer elements in series per tube.

After the last loop, at the end of the feed line, the volume of concentrate is regulated by a regulating valve, or, in special cases, by a positive displacement pump which also functions as a feed pump for further processing.

Control of the degree of concentration can be obtained by means of an in-line refractometer measuring the refractive index in the concentrate as an indirect measure of total solids, by means of flowmeters (ratio-control), or by other in-line measurement. This will be discussed in more detail in the section on automation at the end of this chapter.

For extremely viscous products, it may be necessary to use a positive displacement pump as a booster pump for the last loop to secure the correct flow conditions. In such cases, it is possible to use the energy consumption of the pump to control the level of concentration in the plant. This is possible because of the close correlation between energy consumption and product viscosity.

MF systems

In cross-flow MF systems, the pressure difference between the feed and the permeate side (trans-membrane pressure), must be kept very low, usually less than 1 bar. The concentration polarisation and fouling must be minimised as much as possible in order to avoid secondary membrane formation, which would change the membrane characteristics significantly.

This is achieved through careful control of the trans-membrane pressure as illustrated in Figure 71.

APV has patented a special system where each membrane element is in-

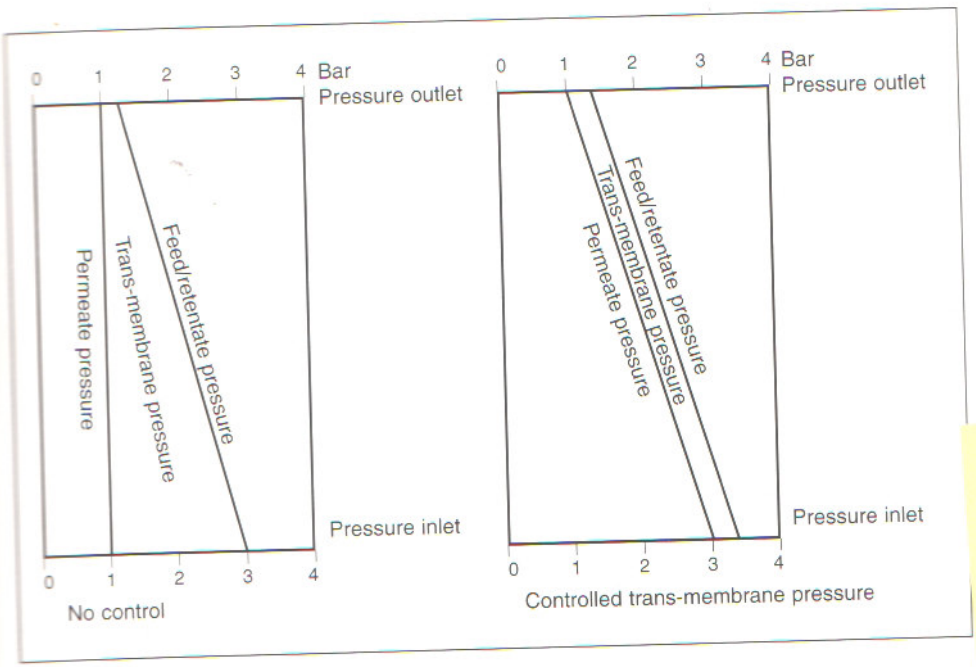


Figure 71: Trans-membrane pressure profile. The key to optimum conditions for microfiltration with ceramic membrane systems is to control the trans-membrane pressure and

stalled inside a stainless steel tube with the same shape as the membrane, and an inner diameter slightly larger than the outer diameter of the element, as shown in Figure 72. This design makes it possible to operate with the same pressure drop along the total flow path in the membrane element, through circulation of permeate on the low pressure side of the membrane elements as illustrated in Figure 73.

The MF plant is based on a continuous system with recycling as described for the UF systems. From a balance tank, the product is fed into a feed line to which one or more MF loops are added.

Each loop consists of a recycling pump and a number of MF membrane elements. The number of elements per loop is limited by the size of the centrifugal recycling pump, which in practice means a maximum of 20-25 m^2 for membrane elements with a channel diameter of 4.0 mm. Each loop is also equipped with a permeate recycling pump as previously explained.

The concentration curve for MF is usually more flat than for UF, which means that the difference in capacity between first and last loop is less pronounced for MF. Also the drop in capacity during concentration from start to finish is lower than that for UF.

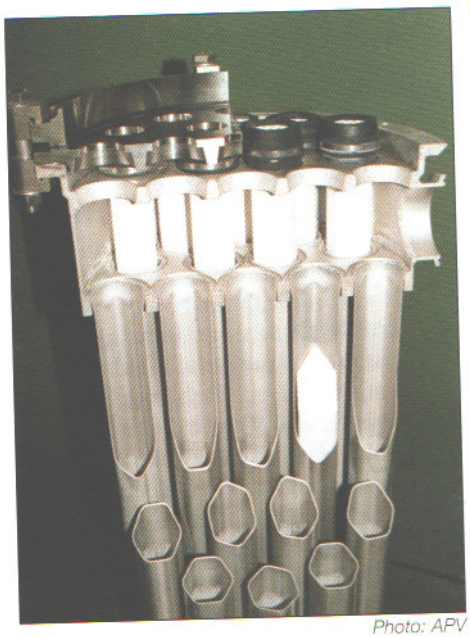


Photo: APV

microfiltration module. A patented design in which a stainless steel tube is fitted around the ceramic membrane element in a way which minimises the dead volume and enables control of the pressure drop on the permeate side.

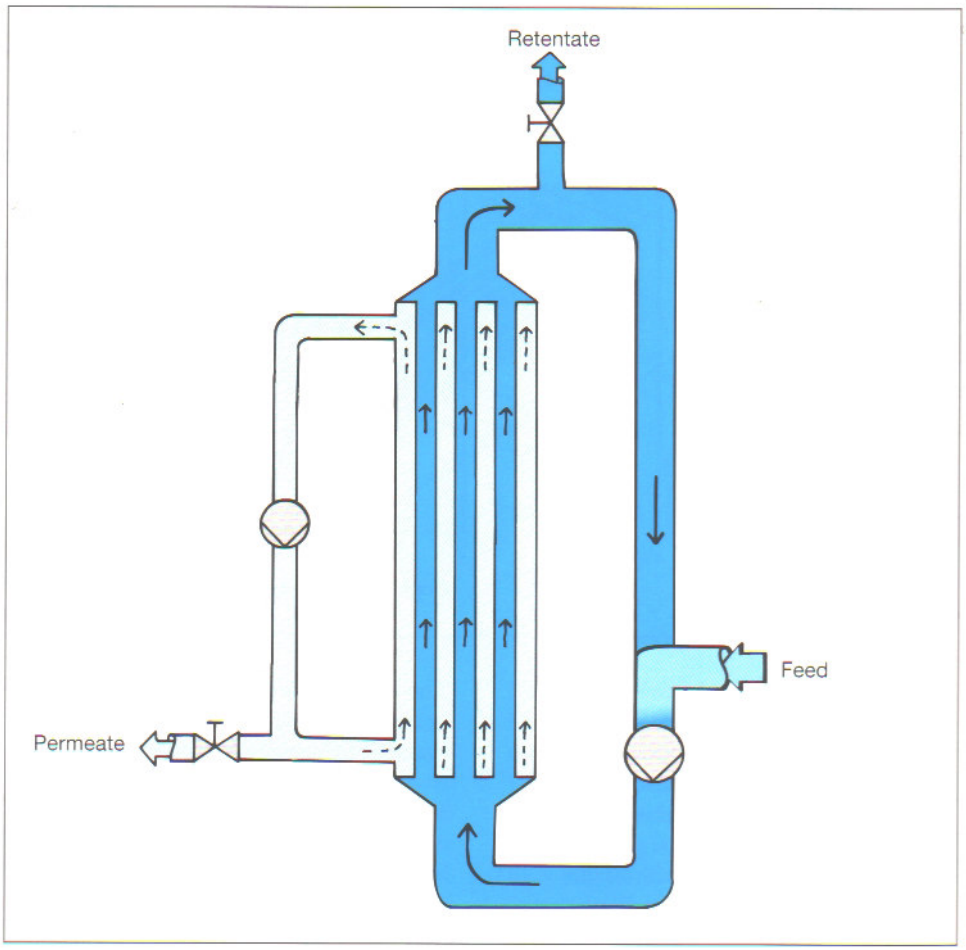


Figure 73: MF loop providing uniform trans-membrane pressure. Permeate is circulated co-currently with the concentrate in order to create a pressure drop on the permeate side equal to the pressure drop on the concentrate side, enabling operation with a constant trans-membrane pressure.

Usually, the MF permeate system is equipped with a control valve system which enables regulation of the pressure in each loop on the permeate side. This makes it possible to operate at a constant capacity throughout a full production run.

A tubular heat exchanger is built into each loop for cooling during production and heating during CIP. Figure 74 illustrates the design of a two-stage MF system. The figure also illustrates the direction of flow on both the concentrate and permeate side.
As an alternative to the control of the trans-membrane pressure, a back pulse or back-flush system may be used. A given permeate volume is pushed back through the membrane at pre-determined intervals.

Electrodialysis systems

The ED process was described in Chapter 3. ED systems can operate both in a batch and in a continuous mode.

A batch system may consist of just one ED stack with the necessary power supplies, feed pumps, and pre-treatment systems. The system is CIP cleaned, and consequently it requires piping and chemical handling. The degree of de-mineralisation is controlled by a conductivity tester. The holding time in a batch

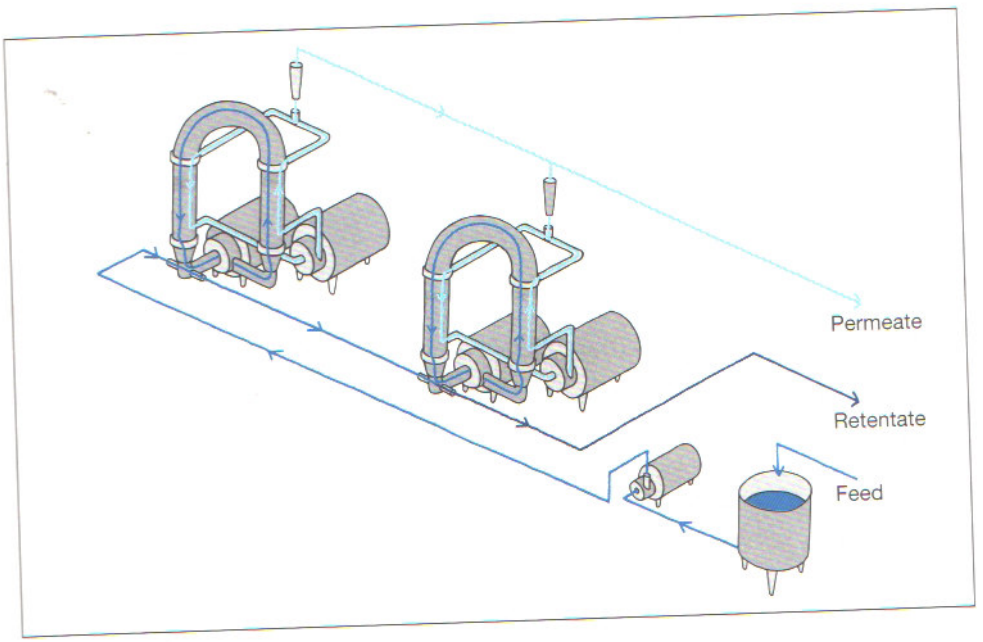


Figure 74: Layout of an MF plant with ceramic membrane elements. The ceramic membrane elements are always placed in a vertical position to avoid rupture.

system may be as long as 5-6 hours, depending on feed and final product requirements. High temperature is advantageous for the process, and consequently operating temperatures in the range of 30-40°C are common. Such high temperatures may present a risk, especially with food products. Bacteriostatic compounds like hydrogen peroxide are therefore added when allowed.

In continuous systems, several ED stacks may be coupled in series, thus reducing the holding time of the product to 10-45 minutes, depending on the product and the requirements for salt removal.

The ED plants, whether batch or continuous, can easily be automated and furnished with automatic CIP systems. A cleaning cycle will last from 1½ to 2 hours, and includes water rinse, cleaning with an alkaline solution (pH at maximum 9), water rinse, cleaning with hydrochloric acid (pH at minimum 1), followed by final water rinse.
As already pointed out, it may sometimes be necessary to remove the membranes from the stack for manual cleaning.

An ED plant uses direct current which requires a facility for regulating the current in the range of 0-185 amp and the voltage in the range of 0-400 volt.

While ED has been used extensively for desalination of brackish water, it has only found limited application in the food and beverage industries, which to some extent is caused by the circumstances stated above.

Electrodialysis reversal or EDR is an ED process in which the polarity of the electrodes is reversed every 15 to 20 minutes. This change in current also reverses the flow direction of the ions. As a result, the salt cells described above become de-salting cells and vice versa (see Figure 12). During the reversal period, deposits and fouling formations are removed and discharged from the membrane. The process is completely automated. During the switch-over, the product water is temporarily discharged, until the required salt level is re-established. EDR makes it possible to use ED to routinely operate at high levels of turbidity and silt density index without fouling. Figure 75 shows a system for ED.

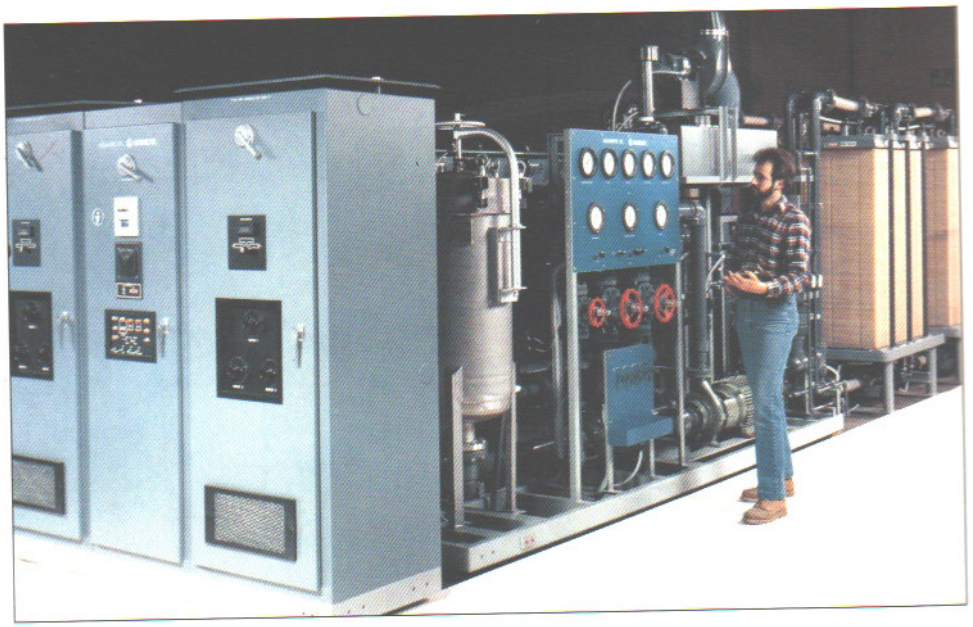


Figure 75: Design of an ED system. The system is characterised by the ED stacks and the power supply.

Ion exchange systems

Traditionally, the design of ion exchange plants involves fixed beds of ion exchange material contained in cylindrical vessels (columns), which are interconnected by pipe work. Each column is maintained in service until it is saturated. The resin is then back-washed with water at a controlled rate to expand the bed and to remove any fine particles resulting from the treatment cycle. Then the ion exchanger is regenerated with the appropriate reagent, any excess of which must be washed free before the column is returned to service.

The various sequences and liquid flows are controlled either by manually operated valves, or, today more commonly, by a PLC (Programable Logic Controller) based control and automation system. The service and regeneration flows are usually in the same direction through the column, hence the term 'fixed bed co-current regeneration'. In such a system, only a fraction of the available resin exchanges at a given time, because the other regions of the column are either exhausted or inactive. Furthermore, it is virtually impossible to regenerate a column completely without a large excess of reagent. Fixed-bed operations are not truly continuous processes, because the treatment cycles have to be interrupted whilst units are taken out of line to be regenerated but this objection is minimised in multi-column plants.

Fixed-bed systems have inadequacies which are largely eliminated by continuous counter-current processes, in which the ion exchanger and solution are cycled counter-currently in the sorption, regeneration and rinsing operations. The various operations may take place in different columns, or in different compartments within the same column. A certain degree of flexibility in a continuous unit is necessary. Therefore, the ideal system is never achieved, but the following advantages are claimed:

- More efficient use of resin capacity
- Smaller total volume of resin required
- Improved regeneration efficiency and corresponding reduction in operating costs

Despite these obvious advantages, the development of continuous ion exchange plants has not been as rapid as expected. This may to a large extent be due to the fact that for water treatment which is still the main application for ion exchange, most of the advantages obtained through the continuous system, can be obtained from the counter-current regeneration techniques using conventional fixed beds.

Chromatography systems

Systems for chromatography are normally evaluated on a much smaller scale. In the pharmaceutical sector, the size of the columns applied can be quite small, from a few 100 ml to a few litres. Systems are built to operate one, two or three columns, and normally consist of the necessary pumps and valves, detection devices, alarm functions and controls needed to operate the plant from a PC-platform. Among the many features of such control systems are normally a Windows environment for easy programming, operation and process updating.

Each step in the process can be independently controlled in order to optimise the operation. Buffers can be switched and various fractions can be collected, based on changes in UV, pH, conductivity, time and volume or on a combination of some of these parameters. Such systems will usually comply with all general manufacturing practices, including documentation, validation, sanitation, data storage and password security.

The QuantaSep 1000 liquid radial flow chromatography system is shown in Figure 76.

Using the Windows-based software, chromatograms can be viewed, and historical chromatograms can be superimposed over each other to monitor run-to-run consistency and reproducibility, product peak, separation, resolution and recovery/yield. Systems consisting of larger columns will basically be designed according to the same principles but due to pump and valve dimensions, each system has so far been designed separately.

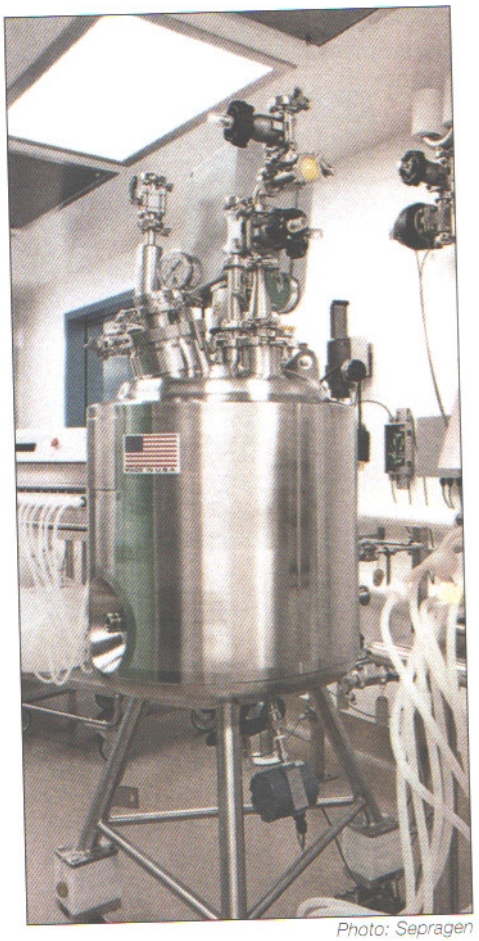


Photo: Sepragen

Figure 76: QuantaSep 1000, a chromatography system for full scale production in the pharmaceutical industry.

System operation

The systems described so far are designed and operated like any other unit operation or plant in industries where such systems are applied. Initially, membrane systems were considered fragile and delicate needing special attention, but this is not the case today. There are of course special considerations in respect of tolerance to temperature, pressure and chemicals as already described, but this is the case for many other processes as well.

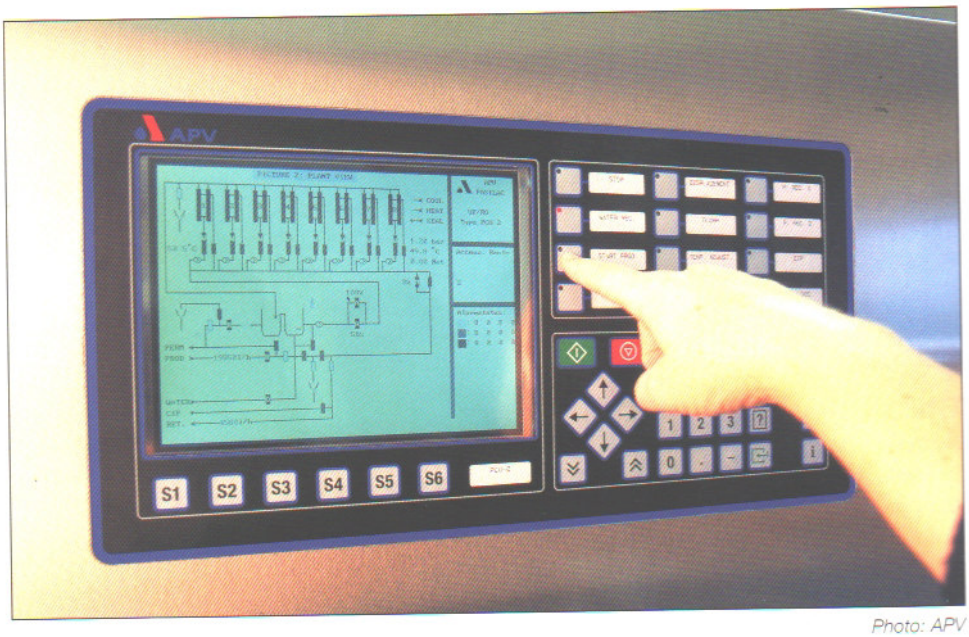


Photo: APV

Figure 77: The control system for a membrane plant can be supplied as a manual, semi-automatic or fully automatic system.

Automation

Membrane-based systems are usually equipped with some type of control system, depending on parameters such as plant size and complexity, number of running hours, safety measures, etc.

The purpose of a control system is to provide a certain level of automation in relation to the number of start/stop functions, cleaning procedures, alarm functions and plant protection. For membrane systems, plant protection is a major issue because of the sensitivity of membranes to excessive temperatures, pressures and pH. It always pays to install recording and alarm equipment and maintain it properly. This may even be a condition for membrane suppliers to provide membranes with warranty.
It is normal to define three levels of control for membrane systems:

Level 1: Manual

Level 2 : Semi-automatic

Level 3: Automatic

Manual control systems may be used for pilot plants and small production plants. The system is based on relays. Pumps have a stop/start button and in order to protect the membranes, a thermostat is included for control of steam and cooling water valves. Various alarm functions are built into the system but, except for 'low feed pressure' which will stop all pumps, only visual signals are given. The manual control system will usually contain some options for addition of a printer, for installation of regulating loops for feed pressure and back pressure, and for control of the concentration level.

Semi-automatic control systems are used for plants equipped with automatic valves and include a number of options for control of the pre- and after-treatment systems.
By means of push buttons, programs for production, CIP, flush out and product recycling can be selected. On the front panel, mimic diagrams of simple flows may be displayed.

The system contains various alarm functions. The signals are not only visual, as described for the manual control system, but here they will automatically bring the plant into a mode which will prevent the membranes from being damaged. The mimic on the front panel displays the alarms and their consequences. This type of control system is commonly used for industrial membrane plants. Figure 77 shows a control system for a membrane filtration plant.

Fully-automatic control systems are used for large and complex plants. It allows pre- and after-treatments of considerable complexity to be included in the system. If required, the control systems are able to communicate with other control systems in the plant. The system is also used where the membrane system is supplied as a part of a complete production plant. All functions are basically automatic and require a minimum of action from the operator. Pumps are always started and stopped in a sequence, which secures the correct stop and start of the plant. At production start, the plant is heated to the operating temperature. At the end of a production run, the system automatically flushes out the plant, with a minimum of product loss.

For CIP, a selection of programs can be installed for the operator to choose between. By constantly displaying the current operation mode with values and set points for the most common parameters, the video screen secures easy control of the system. It is also possible to change alarm set points or analogue regulating loop set points via the screen. It is also possible to connect a printer to the system for recording alarm signals, plant performance data, etc.

Figure 78 shows a production management system for a membrane plant.

On the basis of the ongoing development of so-called intelligent components like pumps, valves and sensors, it is possible to design more intelligent control systems. These systems can provide self-optimisation of the operation to meet constantly enhanced performance crite-

Photo: APV

Figure 78: Production management system. Membrane plants can easily be integrated into larger plants encompassing other processes. Through intelligent automation it is possible to provide sophisticated electronic data for a management information system.

ria, self-diagnostic solutions in case of failure, self-recording of events and parameters and 'open minded systems' which are easy to network. Such intelligent process plants will contribute to the dissemination of molecular separation processes, because the human factor in making mistakes in the operation of plants is significantly reduced.

Cleaning and disinfection

Like all other industrial equipment, the systems must be cleaned at regular intervals. The main purpose is to remove deposits and various fouling substances, and keep the plant in the sanitary condition required for the industry.

Deposits and fouling are liable to reduce plant performance and reduce the quality of the products processed in the system. Hence, it is vital for any application to have the cleaning of the system under complete control at any given time. If the cleaning gets out of control, it may become necessary to exchange the membranes or the resins, which is an unacceptable cost that must be avoided.

Cleaning of membrane systems

There are basically three different types of cleaning methods which apply to membrane systems:

- Hydraulic cleaning
- Mechanical cleaning
- Chemical cleaning

The choice of cleaning method depends on the module configuration, the chemical resistance of the membrane, the construction material of the module and the type of fouling material encountered.

Hydraulic cleaning includes back-flushing, alternate pressurising and depressurising, and by changing the flow direction at a given frequency. This is illustrated in Figure 79. This type of hydraulic cleaning is mainly used for certain UF and MF systems. In order to

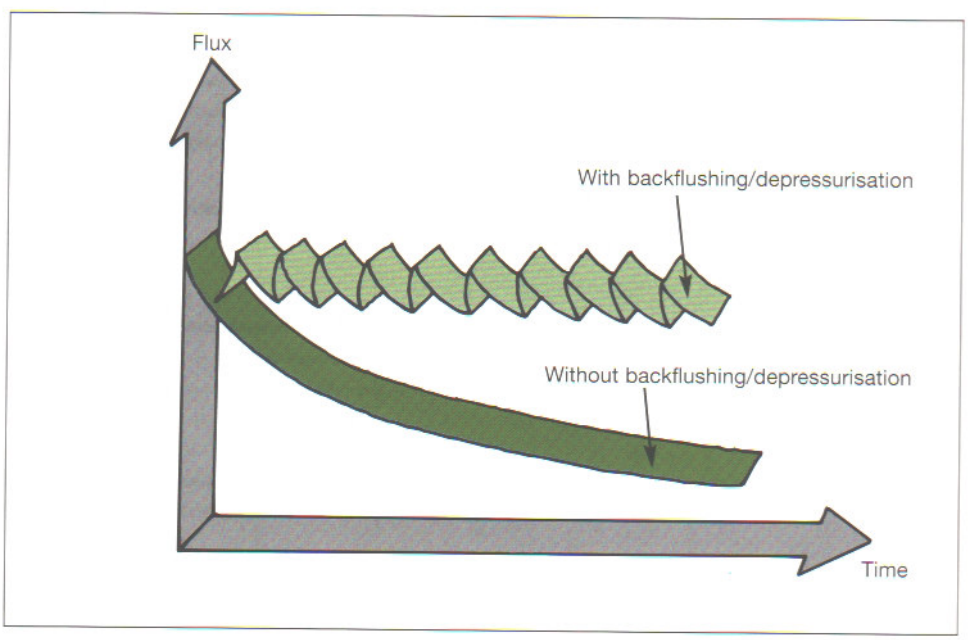


Figure 79: Frequent backflushing/ depressurisation maintains the flux at a constant, stable level.

apply this procedure, the membrane system must be able to tolerate back pressure. This is possible with the ceramic systems where the active layer is strongly fixed to the rigid support tubes.

Mechanical cleaning is mainly applied to tubular systems, where oversized sponge balls are pumped through the system to loosen and push out the fouling material. In some exceptional cases, modules with flat sheet membranes may be taken apart and cleaned manually with a brush. This treatment may easily damage the thin active layer of the membranes, however, it is sometimes applied to electrodialysis membranes which are symmetric in structure and are able to withstand such harsh treatment.

Chemical cleaning is by far the most common way of cleaning membrane systems. It is usually done by CIP, where solutions of chemicals are recycled through the system at a specified temperature and pressure for a certain period of time.

The cleaning procedure for membrane systems normally include the following steps:

- Product removal
- Flushing with water
- Cleaning in one or more steps
- Flushing with water after each step
- Disinfection of the total system

The most common cleaning agents are caustics, acids, detergents, enzymes and complexing agents such as EDTA. Common disinfectants are hydrogen peroxide sodium hypochlorite and sodium bisulphate. In most cases, however, formulated cleaning agents prepared by the suppliers of cleaning agents are applied. Such cleaning agents are used under their respective trade names.

Table 16 shows a typical cleaning procedure for a UF plant in the dairy industry. In order to secure the maximum effect of the cleaning cycles, there are a number of important points to take into consideration:

- *Water quality*. The water used for cleaning must be of the best possible quality. Table 17 states the minimum requirements for the water quality. Sometimes it is necessary to conduct pre-treatment of the water to secure these conditions.

- *Quality of chemicals*. The chemicals used should always be of the best quality and free of any impurities which can cause fouling of the membranes. This is always the case when formulated cleaning agents, tested and approved by the membrane suppliers, are used.

- *Cleaning temperature*. Since the chemical reactions which dissolve the fouling material increase with temperature, the highest possible temperature should be used with due consideration of the tolerance limits of the membranes. When enzymatic cleaning is used, the temperature should be adjusted to the optimum temperature for the specific enzyme system.

- *Pressure*. Operating pressure during cleaning should be kept as low as possible, in order to get the best possible flushing effect across the membrane during cleaning. If the pressure is too high, the water flux becomes very high at the elevated temperature and this will cause the deposits to adhere to the membrane surface.

- *The permeate side of the module*. The flow conditions on the permeate side of most membrane modules are not as good as on the concentrate side. However, the high flux during cleaning contributes to flushing and cleaning of this critical area. Care should be taken to control that the pressure

Table 16: Example of a cleaning procedure for UF plants (sweet whey).

Sequence	Operation	Temperature °C	Duration min.	pH
1	Flushing		until all product is removed	
2	Caustic cleaning	50	20	12
3	Flush out of cleaning agent		10	
4	Acid cleaning	50	20	2
5	Flush out of cleaning agent		10	
6	Caustic + chlorine cleaning	50	40	11.5
7	Flush out of cleaning agent		10	

Check the chlorine content after 8-10 minutes. If the chlorine content is below 100 ppm, top up with hypochlorite to 150 ppm chlorine. Then add hypochlorite at intervals to maintain 150 ppm active chlorine.

Table 17: Requirements for water to be used for CIP cleaning of membrane plants.

Component	Content
Iron (Fe)	<0.05 ppm
Manganese (Mn)	<0.02 ppm
Silicate (SiO_2)	<20 ppm
Chlorine*	<5 ppm
German hardness	<20 °dH
Total plate count at 22°C	<1000 per ml
Total plate count at 37°C	<10 per ml
Coli count	<1 in 100 ml
Fouling index	<3 SDI
Turbidity	<1 NTU

* For organic RO/NF membranes <0.1 ppm chlorine

on the permeate side does not exceed the pressure on the concentrate side, since this may cause rupture of the membranes in certain types of modules.

- *Water flux*. It is common practice to check the water flux of the plant after it has been cleaned, since re-establishment of this parameter is a practical way to make sure that the plant has been properly cleaned. The water flux should be recorded on a daily basis.

Membranes are usually supplied with a warranty which is subject to correct operation and cleaning of the plant. In order to have documentation, in case the question of membrane warranty becomes

pH
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ppm, top up in 150 ppm

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f the plant. In
tion, in case the
arranty becomes

an issue, it is always advisable to keep good records of the production and cleaning cycles.

Cleaning of resin systems

The cleaning and maintenance of resins is primarily achieved through the regeneration and back washing cycles and subsequent flushing with water. The sensitivity of resin materials to chemicals and temperatures depends on the chemical composition of the resins. In many respects they resemble membrane materials.

Resins in continuous operation are subjected to extreme changes in pH during regeneration, which minimises the problems of biological growth in the columns. Most biological growth problems are caused by inactivity of the resins during extended storage. In order to minimise the potential for bio-fouling, inactive systems can be stored in a biostatic solution such as 2% NaOH.

In cases where biological problems have already occured, the use of a specific procedure based on peracetic acid treatment is recommended. Since anion and cation resins behave differently when exposed to changes in pH, the procedures must be adjusted to the chemical structure of the specific resin.

Resin storage should take place at a low temperature (above freezing) and with an antibacterial (as described above) preservative added, which will not damage the active groups of the resin or the resin backbone itself.

13 Laboratory and pilot systems

So far the description of molecular separation processes has mainly referred to large-scale industrial systems. In this chapter, laboratory and pilot systems are briefly described. Whether dealing with membrane systems or resin-based systems, it is always a challenge to predict the performance for various applications and to scale up to larger capacities.

Certain applications, like desalination of sea water using RO or demineralisation of tap water for boiler feed using ion exchange, are so well documented that the dimensioning of large scale plants is straightforward.

In many cases, however, it is necessary to perform laboratory and/or pilot plant tests, and this is particularly true for molecular separation processes. Hence, the design of appropriate lab and pilot plant equipment is essential for successful exploitation of the many possibilities these processes offer.

It is not possible to give a complete review of all types of plants within this area, but a few examples of systems are shown in Figure 80-85.

Figure 81 shows a plate & frame type UF pilot plant used for concentration of high-viscosity products like quark and cream cheese. This type of equipment is mostly in the high concentration part of cream cheese plants whereas spiral-wound systems are used in the lower concentration end of the plant.

RO/NF/UF/MF pilot plants can also be combined in one pilot plant as shown in Figure 82.

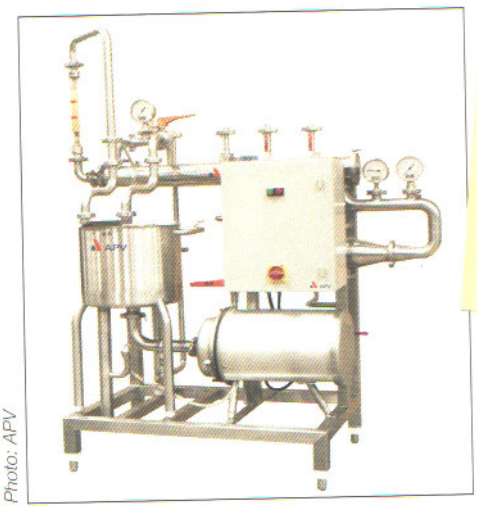


Photo: APV

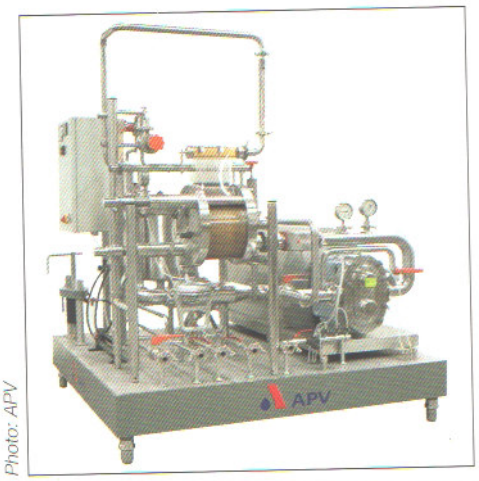


Photo: APV

Figure 81: APV Pilot Plant Plate & Frame system M37 with flat sheet membranes. The plate stack contains from 1.65 m^2 up to 6.6 m^2.

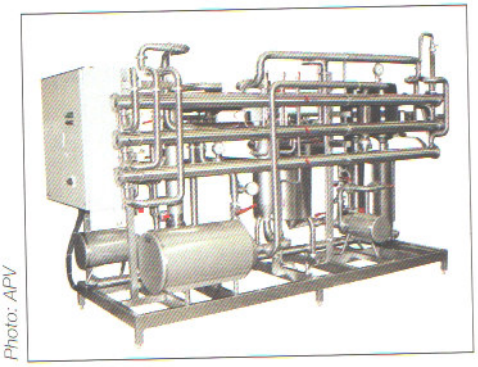


Photo: APV

Figure 82: Multi-Technology Pilot Plant. The plant is applicable for RO, NF, UF and MF SW membranes.

Figure 83:
APV Pilot plant with spiral-wound and ceramic elements. The system may contain 2.5 – 16.5 m^2 spiral and 1.68 m^2 ceramic membrane area.

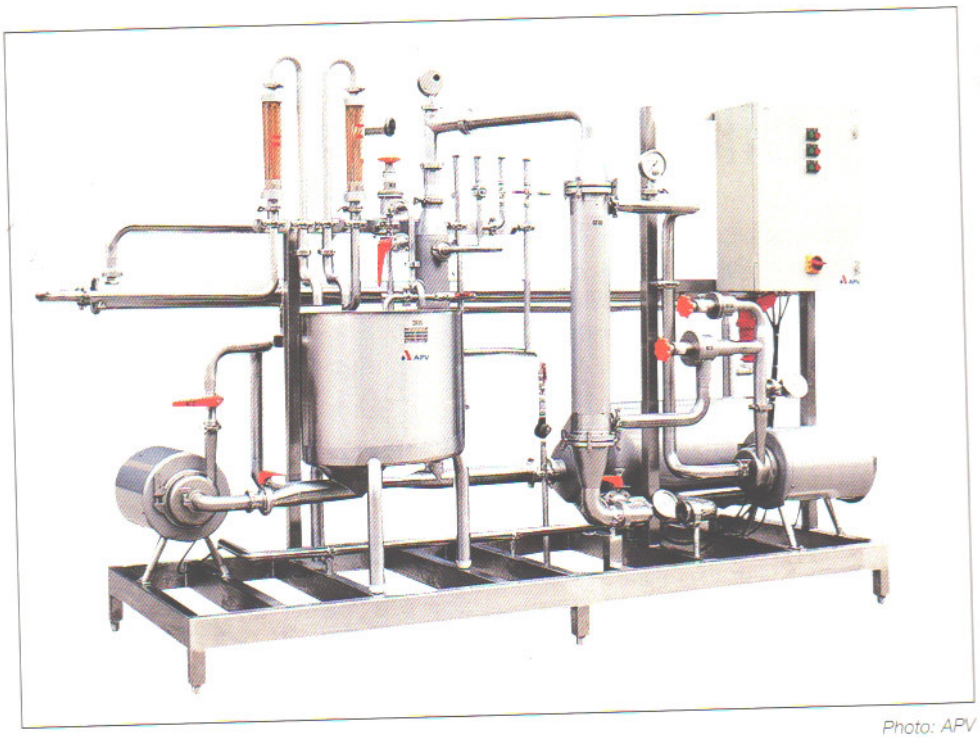


Photo: APV

Figure 84:
Quantasep lab system for radial flow chromatography. A complete system for operating an RFC column automatically and providing electronic data.

Photo: Sepragen

Figure 85:
Amersham Pharmacia Biotech chromatography system. A complete test unit, fully automated with electronic data communication.

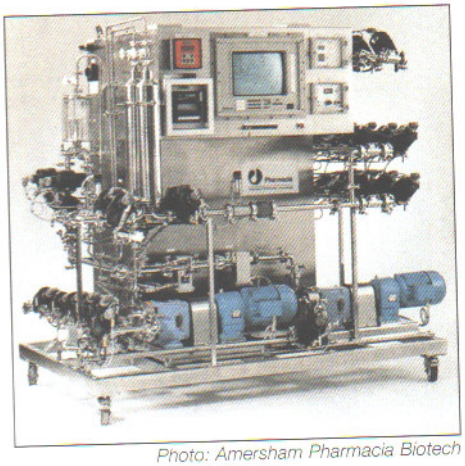


Photo: Amersham Pharmacia Biotech

14 Applications of membrane filtration

Applications of molecular separation processes cover a very wide range of industries. It may be true to say that there is hardly any industry where these processes are not playing a role in one way or another.

Water treatment has paved the way for both RO, UF, ED and IE. It is on the basis of results from successful applications for water treatment that these technologies have developed into food, dairy, beverage and industrial applications.

Photo: APV

Water treatment

The elemental need for water is a powerful factor in the world today. Increasing population growth and increasing pollution create a growing demand for new water supplies. The list of factors creating the increasing demands is long and still growing, but some of these factors, are:

- Population growth
- Increasing number of resorts in areas with insufficient water supplies
- Intensification of agriculture increasing the use of fertilisers and pesticides
- Increasing pollution of seas, rivers and ground water through industrial, agricultural and urban activities
- Increasing water consumption per capita in the industrial world
- Air pollution causing acid rain
- Falling ground water level due to excessive consumption of water
- Growing number of floods and other weather forced catastrophes
- Growing number of droughts in many parts of the world
- Growing agricultural activities in desert areas like the Middle East
- Major improvements in methods for measuring even very low polluting concentrations of chemicals

These are just some of the reasons why water is becoming a scarce resource to a much larger extent than in the past. Molecular separation can solve many of these problems, however, at a cost which has to be justified, through the benefits exposed, to the consumers and to the population in general.

One of the areas of the world where the water situation is very critical is in the Arabian Gulf countries. Table 18 illustrates how the demand for water is expected to increase by the year 2020, compared with the actual consumption recorded in 1990. The values show that there is a large installed base of desalination capacity, and that this is expected to supply an even larger part of the total consumption in the future. The values also show that reuse of water is increasing as a way to secure water supplies, also in this part of the world.

Sea water desalination

Before RO was invented, sea water was desalinated through evaporation and re-condensation, and a large number of such plants are in operation around the world. Such plants are designed as multi-stage flash systems, also called MSF plants. Due to the high specific heat for evaporation of water, this is a very energy-consuming process. Furthermore, because of the salt, the process takes place in a very corrosive environment,

Table 18: Present and projected water demands in the Arabian Gulf countries.

Demands/resources	Consumption 1990 Mm^3/year	Estimated demand 2020 Mm^3/year	Expected annual increase %
Water demands:			
Domestic	3,400	6,100	2.6
Agricultural	18,000	21,000	0.5
Industrial/social	350	750	3.8
Total	21,750	27,850	0.9
Water resources:			
Natural ground and surface water	19,400	24,200	0.8
Desalinated water	2,100	3,000	1.4
Reused water	250	650	5.3
Total	21,750	27,850	0.9

and very corrosive-resistant construction materials have to be used. This requires a high level of investment and high maintenance costs. The plants are relatively complex in design, and require fairly skilled operators.

RO takes place at an ambient temperature, and the water need not go through a phase change, meaning that the problems with MSF plants are basically avoided when this process is used.

The challenge has been to manufacture high flux membranes sufficiently tight to reject more than 99% salt, which is required for desalination of sea water in one step. The membranes also need to be sufficiently robust to withstand long operating times. This was a major problem when leaking membranes caused too high a salt content in the desalinated water.

The membranes used today fulfil these requirements, and especially the development of the thin film composite membranes was a major step towards single-stage RO desalination plants. In many cases, two-stage plants are used where the permeate from the first stage is desalinated with a more open, high flux membrane in a second stage. This enables desalination of sea water with extremely high salt content (>4.5%), which is found in many parts of the world.

The systems used are in most cases spiral-wound or hollow fine fibres, but plate-and-frame may be used for more difficult types of water with a high content of calcium, or other severely fouling material.

Pre-treatment of the sea water prior to desalination is essential and depends on the RO system used and the size of the plant. For small installations, some of the pre-treatment may be omitted to save investment costs, and be substituted by more frequent cleaning of the system.

Brackish water desalination

Brackish water contains less salt than sea water, and in that respect it is easier to handle, due to a lower osmotic pressure.

In many cases, however, brackish water contains more fouling material due to its origin.

Ground water may contain high levels of calcium, sulphate, silica, iron and manganese, which easily form precipitates on the surface of the membranes, reducing flux and rejection.

Surface water may contain large amounts of organic material causing very unpleasant fouling, which may be difficult to remove even by harsh cleaning. Hence, pre-treatment becomes a major condition for trouble-free operation of brackish water desalination plants. In order to design the water plant, a water analysis is required. Table 19 is an example of such a water analysis, giving the composition and content of dissolved salts, as well as information on turbidity, suspended solids, etc.

The pre-treatment typically contains the following steps:

- *Water intake*. Raw water is pumped through a 100 µm screen to a sand filter, where large particles and suspended solids are removed. In case of large contents of iron or manganese, air is blown into the feed to the sand filter by means of a compressor in order to precipitate iron and manganese hydroxides, which are subsequently removed in the sand filter

- *Chlorination and de-chlorination*. When there are large amounts of bacteria in the water, it may be necessary to add sodium hypochlorite to disinfect the water in order to avoid bacteriological problems in the RO plant. Since membranes are sensitive to even small amounts of chlorine, the water can be filtered through a column of activated carbon in order to remove the remaining chlorine content

- *Safety filtration*. It is common to have a safety filter after the sand filter, usually 25 µm, to protect the membrane system

- *Antiscaling*. Depending on the water composition, various types of chemicals may be added. Acid is used to adjust pH to a level where precipitation of calcium carbonate is avoided. Normally, sulphuric or hydrochloric acids are used, and the addition takes place with metering pumps controlled by in-line pH measurement.

  For high levels of hydrogen carboate, it may be necessary to remove carbon dioxide by blowing air through the water after the pH adjustment. Polyphosphates are also used in some cases to form soluble complexes with calcium. Other complexing agents like EDTA and citric acid are also used

- *Temperature adjustment*. The water flux increases with temperature, and sometimes it pays off to heat the water prior to entry the RO plant, in order to get a better utilisation of the installed membrane area. However, the temperature limitation of the membranes has to be watched, and it must be taken into consideration that some heating takes place in the RO plant, which in extreme cases may require that the water is cooled

- *Ultraviolet radiation*. Sometimes UV light may be used to kill bacteria prior to treatment in the RO plant. This will also make it possible to mix raw water with the permeate in cases where the salt content is lower than required for drinking water purposes.

The RO plant is usually designed as a continuous process over a number of stages with recycling. The pumps used are multi-stage centrifugal pumps. This

system makes it possible to adjust the water utilisation, and secures smooth operation even with minor variations in the feed water quality.

The pH in the permeate is usually around 5.0, and this may be too low for drinking water. The low pH can be compensated for by controlled addition of sodium hydroxide, sodium carbonate, or by passing the water through a re-hardening filter containing lime or similar components. The re-hardening also contributes to an improved taste due to the take up of calcium and magnesium ions.

Table 20 shows the raw water and product water analysis from a desalination plant in the Middle East. Table 21 shows the plant performance data for the same plant. Figure 86 shows a water desalination plant with spiral-wound elements.

Table 19: Typical analysis for well water with a high salt content.

Sodium	ppm	290
Calcium	ppm	234
Magnesium	ppm	72
Chlorine	ppm	0.0
Potassium	ppm	43
Iron	ppm	0.1
Manganese	ppm	0.0
Silicia	ppm	8.9
Sulphate	ppm	560
Chloride	ppm	640
Alkalinity (HCO_3)	ppm	100
Total dissolved solids	ppm	2,000
Suspended solids	ppm	1.0
Permanganate value	ppm	4.7
Plugging index	ppm	1.0
Total hardness (CaO)	°dH	49
Turbidity	NTU	0.8
Conductivity	µS/cm	3,060
Temperature	°C	24
pH		7.7

Table 20: Raw and product water analysis for an RO water plant in the Middle East.

Component		Raw water	Product water
Sodium	ppm	1,050	35
Calcium	ppm	450	7
Magnesium	ppm	148	3
Chlorine	ppm	2,057	74
Potassium	ppm	-	-
Iron	ppm	0.15	0
Manganese	ppm	0	0
Silica	ppm	14	0.3
Sulphate	ppm	865	11
Alkalinity (HCO_3)	ppm	214	6
Total dissolved solids	ppm	5,491	160
Conductivity	µS/cm	7,800	265
pH		7.9	5.5

Ultra-pure water

In many industries, the quality of products and processes depends on access to high quality water. A well-known example is the power industry, where seasonal variations in the colloidal silica content of boiler feed water have a pronounced effect on the blow down rate, which prevents excessive scaling on the heating surfaces in the boilers.

The electronic industry is very dependent on high quality water for the production of integrated circuit chips. In hospitals, the water used for haemodialysis needs to be pyrogen-free, not to damage the patients.

Historically, distillation has been used to produce such water. As previously described, this is an energy-consuming process, but it also means that the water needs to be stored for a considerable time. Storage of distilled water may lead to deterioration of the quality by bacteriological activity. Furthermore, distillation may not remove all of the low molecular weight compounds which have boiling points lower than water.

Hence, the introduction of membrane filtration for water treatment was a welcome opportunity to solve some of these problems. RO reduces the mineral content

at a lower cost than ion exchange. Even though the same purity and low conductivity of 0.2 µS/cm required for high-pressure boiler feed water cannot be obtained by RO, the bulk of the minerals can be removed, and the final water quality can be obtained by using a mixed-bed ion exchanger as a polisher. This reduces the cost of regeneration dramatically. RO furthermore removes all particles, and reduces the content of bacteria and pyrogens significantly.

Pyrogens in water present a problem in certain applications. Pyrogens are defined as substances causing a temperature rise (fever) in living organisms, when injected. Most pyrogens are lipopolysaccharides from bacteria cell walls with a molecular size in the order of 20,000 or more. They are not removed by autoclaving or MF, but are successfully removed by RO, NF, or tight UF membranes.

Water for medical use, e.g. for injection, or water for haemodialysis must be pyrogen-free, and this is normally achieved through RO.

Water for injection is strictly regulated by the authorities. In Europe, the European Pharmacopeia prescribes such water to be produced by distillation. However, within the US Pharmacopeia, water for injection may be produced either by means of distillation or RO, and in Japan, UF is also accepted as a means to produce water for injection.

Due to the potential risk of failure of membranes, it is common to use 'double' RO, where the second treatment provides an additional barrier for bacteria and pyrogens. In practice, plants for production of purified water consist of a combination of processes, including activated carbon filtration, IE, MF, RO, UF and UV treatment.

Inlet pressure	bar	29
Outlet pressure	bar	21
Feed water	m^3/h	15.4
Product water	m^3/h	10
Reject water	m^3/h	5.4
Pre-treated by-pass	m^3/h	1.0
Total product water	m^3/h	11
Total water recovery	%	71
Operating temperature	°C	27-50
Final product water quality	ppm NaCl	<400

Table 21: Plant performance data from a brackish water desalination plant.

Figures 87, 88, and 89 illustrate three different types of water treatment plants producing purified water using combinations of the processes referred to above.

In the pharmaceutical industry, UF may also be used to remove pyrogens in the production of pharmaceutical products. This is possible if the product molecule is sufficiently small to allow the use of a UF membrane, which rejects the pyrogens, but allows the product molecule to pass through.

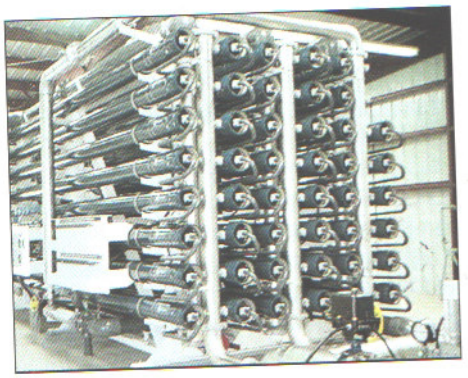


Figure 86: A spiral-wound RO water desalination plant.

Figure 87: Conventional ion exchange system for production of pure water.

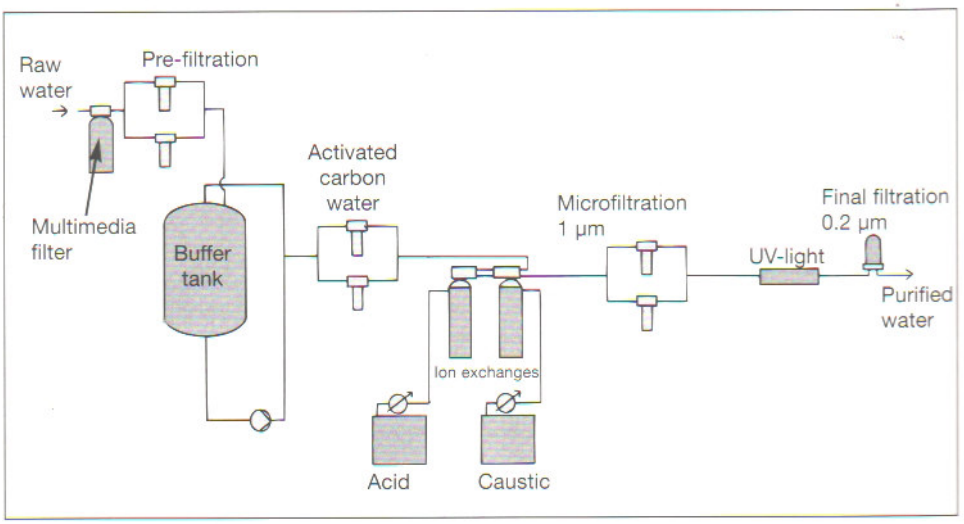
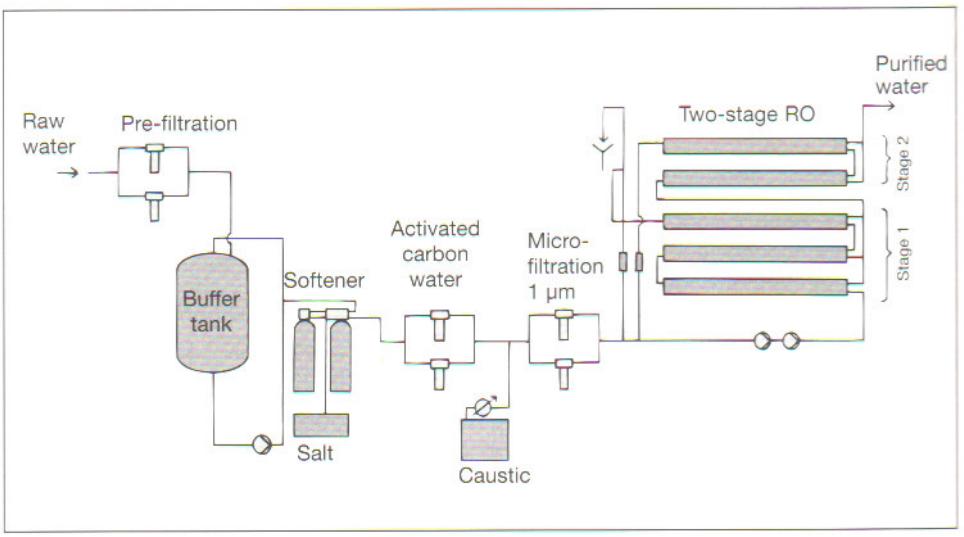


Figure 88: Water purification system using two-stage RO.



Waste water

Waste water is a very broad term which must be sub-divided.

Municipal waste water is largely composed of organic matter present as soluble, colloidal and suspended solids, and it is basically waste water from households. The pollution is normally proportional to the number of inhabitants in a specific community. The treatment usually consists of a biological treatment, sometimes followed by a treatment for removal of nutrients and inorganics, known as tertiary treatment.

Industrial waste water varies from industry to industry, and depends to a large extent on feed product, process, and plant design. Consequently, the treatment methods vary considerably, depending on plant design and operation, and on the requirements of the local authorities for the accepted level of outlet from the plant.

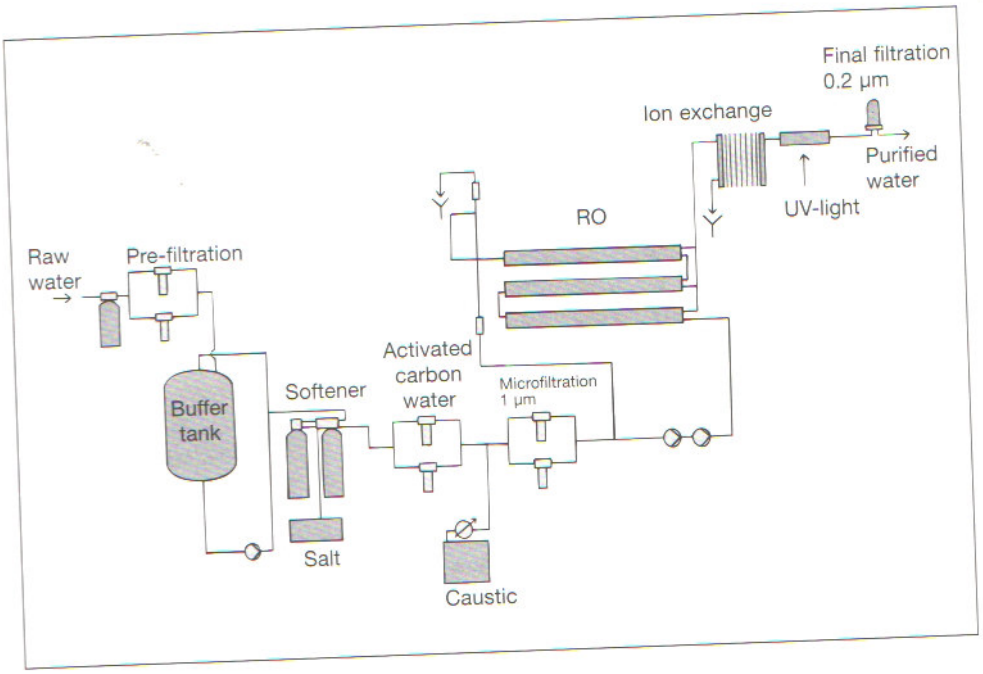


Figure 89: A system using reverse osmosis and continuous deionisation for the production of pure water.

Over the years, it has become more common to look at the recovery of some of the components in waste and outlet streams. This makes it possible to recover valuable products and possibly reuse the water, thus reducing the total water consumption.

Molecular separation processes may be used in all these areas, but they really come into their own, in the area of product and water recovery. The subject of product and water recovery will be dealt with in the next section.

RO can be used for tertiary treatment of municipal waste water after biological treatment has removed most of the organic material. The permeate from an RO plant is very clean, free of suspended solids, bacteria, viruses, minerals, and most of the low molecular weight compounds. In some instances, this water may be led back to the ground water, thus serving as a water conservation measure.

The leach water from waste water disposal sites has become a serious problem. By using RO, it is possible to concentrate the solids in the leach water up to a solids level of 3-5%, leaving 80-90% of the leach water as pure water, which can be disposed of in the sewer without further treatment.
The concentrate can be evaporated, dried and disposed of in a form which prevents any further impact on the environment.

Product and water recovery

In the food and dairy industries there is an increasing focus on effluent discharged into the sewage system. The constantly increasing effluent charges have moved the focal point from end-of-pipe treatment to prevention of pollution.

In the food industries, the pollutants in the waste streams are often product residues. By using membrane filtration, such waste streams can be concentrated and separated into two streams:

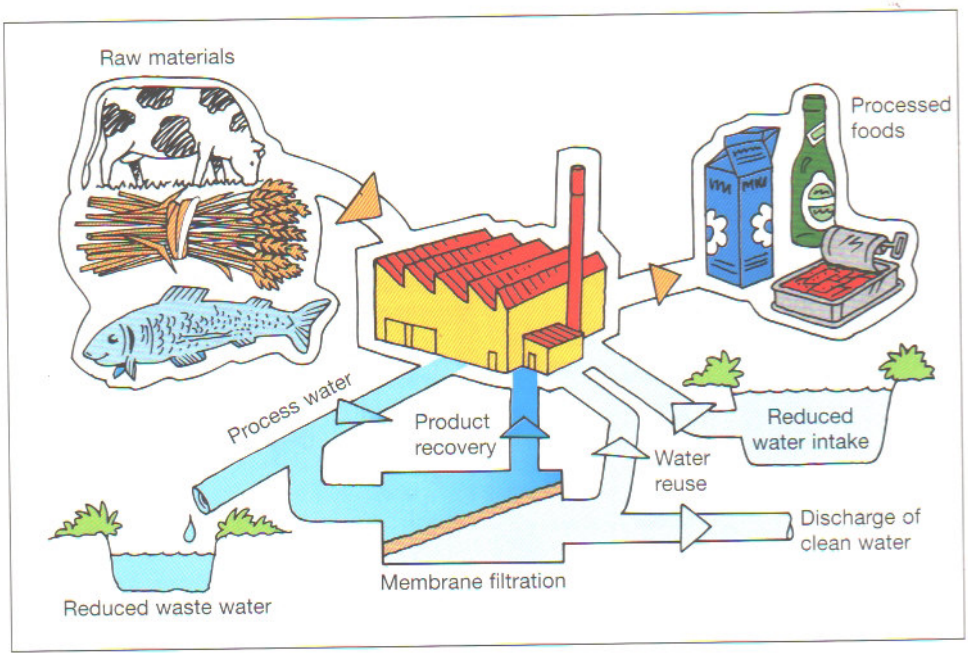


Figure 90: Reuse of process water and product residues. The general aim is to minimise the overall water consumption and environmental impact.

- A concentrate containing the recovered products in a concentrated form
- The permeate consisting of purified, reusable water

Membrane filtration is a purely mechanical separation process with no additions of chemicals to the product. Typical concentration factors are 10-20 times, which means that 90-95% of the waste stream is separated into reusable water. The remaining 5-10% is the concentrate with a high content of solids, which facilitates easy handling and reuse.

Environmental applications for membrane filtration technology are found in all industries where water is used to wash, cook, extract, or transport products. The closer to the source the water is treated, the better the possibility of recovering high-value contaminants such as proteins and carbohydrates. The main objectives are:

- Recovery of valuable product residues (proteins, carbohydrates and flavours) from process water
- Concentration of BOD/COD components, resulting in water that is acceptable for discharge
- Reduced consumption of fresh water by continuous recovery and recycling of process water
- Recovery and reuse of CIP chemicals such as caustics and acids

The general principle of water and product recovery is illustrated in Figure 90. This concept is increasingly applied in areas like:

- Dairy industry
- Beverage and brewing industry
- Potato starch industry
- Fish processing industry
- Vegetable processing industry
- Slaughter houses
- Other food-related industries with large water consumption

Tests from a herring filleting factory have proven that NF, in combination with centrifugation as a pre-treatment,

		Feed to centrifuge	Feed after centrifuge (25 m³/h)	NF permeate (23 m³/h)	NF concentrate (2 m³/h)	Relative reduction %
Total solids	%	1.10	0.60	0.23	5.00	79
Suspended solids	mg/l	6,000	3,000	0	38,800	100
Fat/oil	mg/kg	2,800	1,000	0	12,900	100
COD	mg/l	15,000	7,000	500	84,500	97
Nitrogen	mg/kg	1,150	600	115	6,400	90
Phosphorus	mg/kg	150	85	16	900	89

Table 22: Results from centrifugation and nanofiltration of process water from herring filleting.

is the optimal solution for treatment of the waste water. The purified waste water can be used for selected cleaning purposes, or it can be discharged. The concentrate from the process can be reused, e.g. as animal feed. The results of NF of the waste water are shown in Table 22. The values may vary considerably from day to day, and over the year, depending on the concentrations of the various components in the process water.

As a means of solving its waste water problems, the fish industry now views membrane filtration as an integral part of the solution to its future plans for water conservation and product recovery.

Dairy industry

During the past 25-30 years, membrane filtration has been established as a common unit operation both in traditional dairy processing and for totally new and exciting applications, enabling the production of new, value-added products.

The dairy industry may be characterised as the industry outside the water treatment industry which has, most successfully, been able to put membranes to work for the benefit of the industry and its customers.

Protein concentration and fractionation

Whey used to be considered as a waste product from cheese production, without value and difficult to dispose of. Direct dumping in the sea, spraying on fields, or at best feeding it to cows, were the most common ways of disposal.

Membrane filtration has changed this picture completely, and today whey is a valuable by-product leading to high value-added products like whey protein concentrate (WPC), isolated whey protein (IWP) and even purified α-lactalbumin and β-lactoglobulin. The raw material for such products is either sweet whey or acid whey. Sweet whey originates from cheese production or rennet casein, whereas acid whey is derived from various types of casein precipitated by pH manipulation, as well as production of fresh cheeses like quarg.

Figure 91 illustrates the many possibilities that membrane filtration offer for converting whey into high value-added products. It also illustrates where electrodialysis, ion exchange and chromatography fit into the processing map. Other separation processes like centrifugal separation, evaporation, crystallisation and spray drying are all part of complete whey processing. This is truly a perfect example of how various separation technologies work together in a complimentary way.

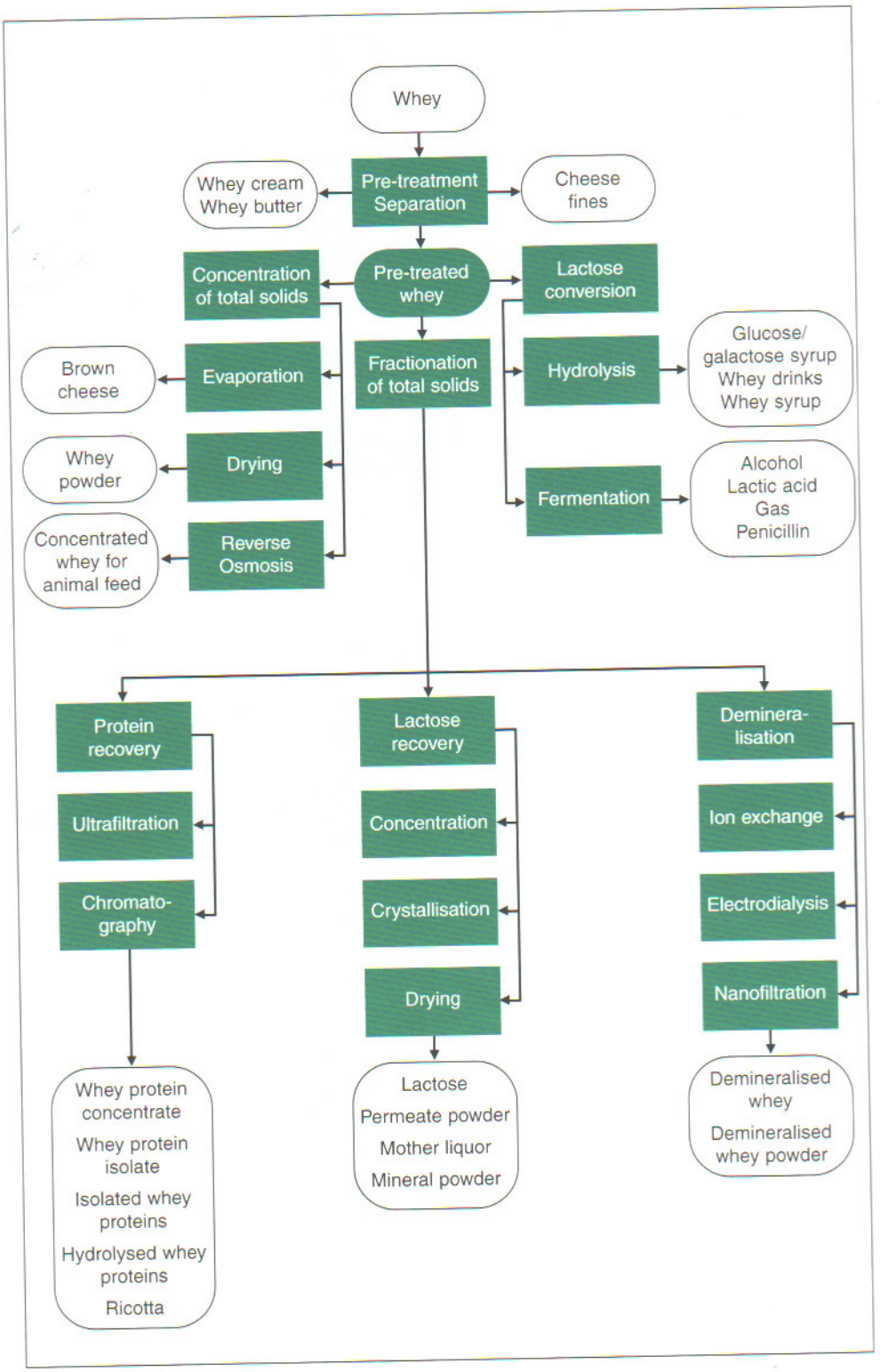


Figure 91: Adding value to whey. There are many opportunities for recovery of valuable components from whey.

Figure 92 illustrates the production of WPC powder from sweet whey.

MF can be included as an option for removal of both bacteria and fat, thus contributing to an improved quality of the final product.

A combination of UF and diafiltration makes it possible to produce WPC with from 35 to 85% protein in the total solids, compared with whey powder with only 12-15% protein. Using MF in the pre-treatment makes it possible to produce WPI with 90% protein in the total solids. WPI can be produced by combining various processes, which will be described in Chapter 15. The concentrate from MF contains some protein and it can be used for production of WPC with 35% protein in the total solids.

The high value added products produced from whey are important sources of protein for a great many food products, ranging from processed meat and sausages, over health foods, to beverages and confectionery.

Milk protein concentrate (MPC) is produced in a similar way to WPC, but is based on skimmilk as the raw material for the UF process. Consequently, the proteins in the powder consist of both casein and whey proteins. The quality and functional properties of MPC are determined by the types of production steps and their combination. The UF pro-

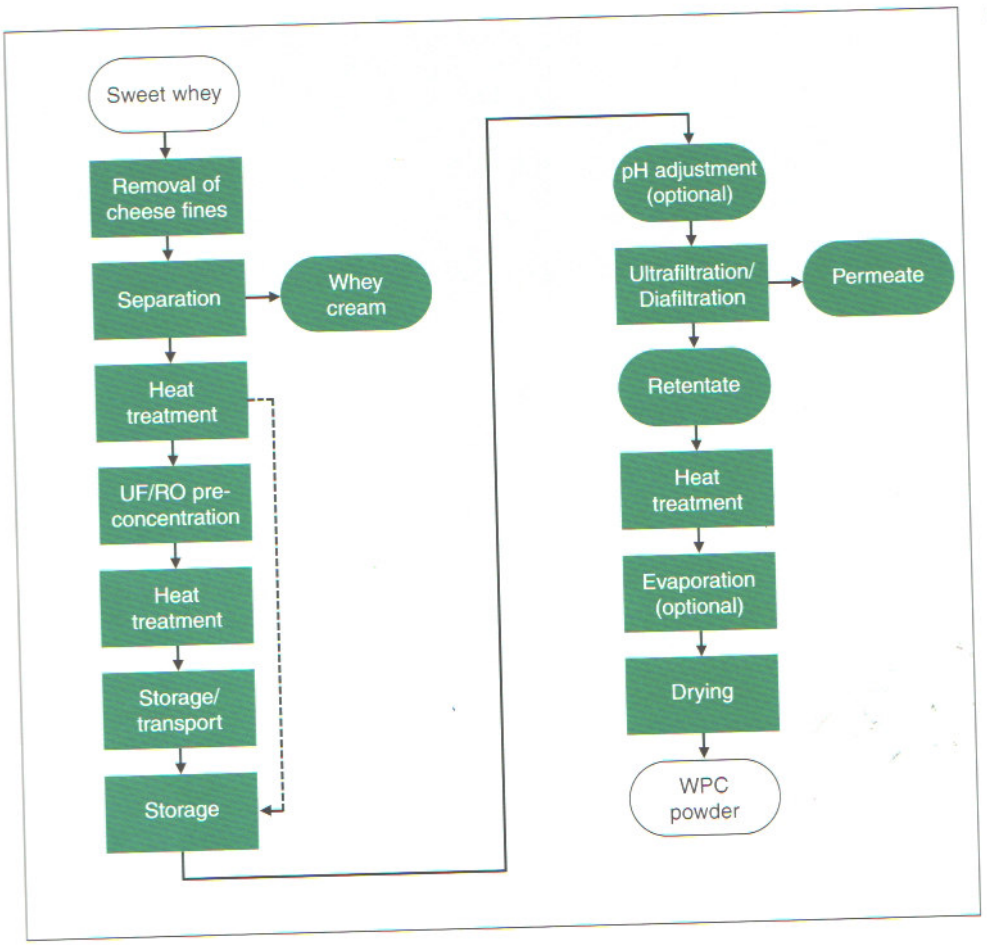


Figure 92: Processing steps in the production of WPC from sweet whey.

Photo: APV

Figure 93: APV Spiral-wound UF plant. The spiral-wound membrane system is now standard in dairies all over the world.

cess determines the composition, whereas the pasteurisation, MF, evaporation and drying determine the thermal load and the bacteriological quality of the powder.

The membranes used for the production of protein concentrates are normally of the spiral-wound configuration, but both hollow fibre, ceramic, tubular and plate-and-frame systems, may be used. Figure 93 shows a spiral-wound UF plant for whey protein recovery.

Protein standardisation

The centrifugal separator made it possible to separate fat from milk. By adding back a calculated quantity of milk fat to the skimmilk, it became possible to standardise the fat content in milk. This is today common practice in most countries, both for the production of manufactured milk products and for market milk.

Originally, fat was considered to be the most valuable component in milk, but in recent times, the protein content of milk has become increasingly important, and today many countries pay farmers according to both fat and protein content. In many countries, the protein content may vary substantially during the year, and UF is the only technology available for protein standardisation of milk without using 'additives' such as milk powders, casein, WPC or lactose.

Photo: APV

Using UF, whole milk or skimmilk is separated into a protein rich fraction (concentrate), and a protein free fraction (permeate). By removing a pre-calculated amount of concentrate or permeate from a certain volume of milk, the protein content can be decreased or increased within wide limits around the normal, average protein content as illustrated in Figure 94. This process is increasingly used for:

- *Market milk* in order to provide consumers with a uniform quality product, independent of seasonal changes, and to help the dairies optimise the protein utilisation
- *Special products* where the protein content is increased, compared to the normal milk composition. This is done to produce milk with additional health benefits, and superior taste and quality
- *Cheese milk* where standardisation of the protein content reduces the need for seasonal adjustments of the cheese-making process, and improves the yield per cheese-making vat. Also, the cheese quality is improved, and it is possible to increase the utilisation of the cheese-making equipment
- *Fermented products* where protein standardisation improves product quality and enables an increased solids level in the products
- *Milk powder* where protein standardisation provides a more uniform powder quality, and excess protein can be used for other purposes

From a membrane design point of view, the plants are fairly simple due to the relatively low degree of concentration. Most types of membrane can be used, but the spiral-wound type is the most common today.

Cheese processes

Next to the production of WPC, the manufacture of cheese by means of UF is

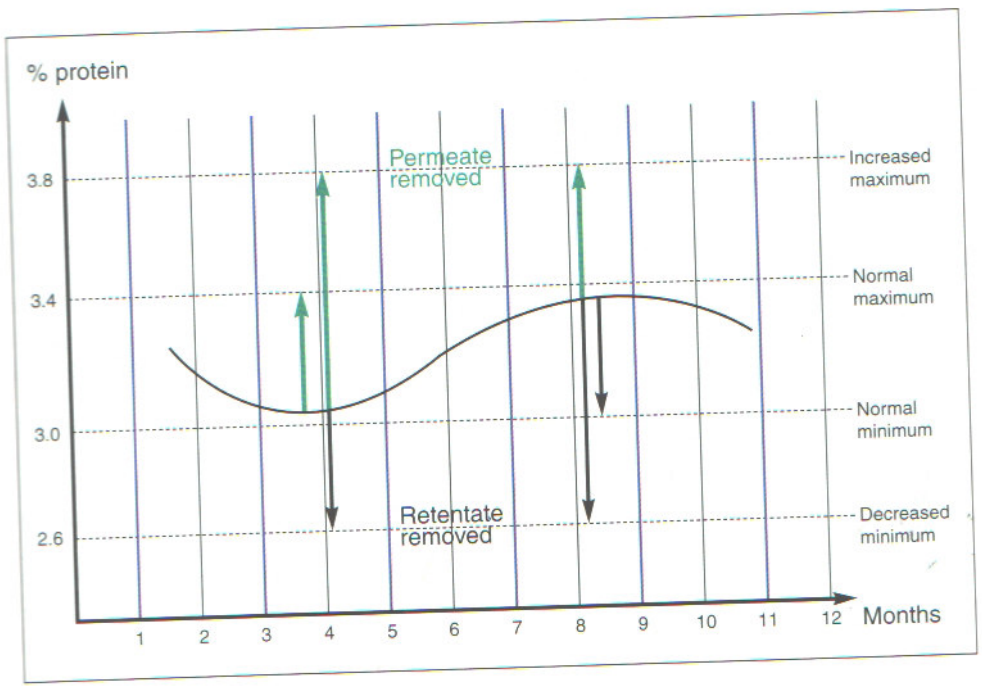


Figure 94: UF technology offers standardisation of the protein level within wide limits.

probably the most widespread application of membranes in the dairy industry. The drive behind the development of membrane filtration based cheese processes is the desire to obtain a continuous process with an increased yield compared with conventional cheesemaking. The higher yield is obtained by including the whey proteins in the cheese. However, this may also have some negative effects, such as a change in consistency, a change in some functional properties, and slower ripening.

Overall, the development of UF-based cheesemaking processes has been very successful, with cast Feta, Quarg, and Cream cheese as some of the most positive examples. However, it has also been proven that for certain higher solids, ripened cheeses, the higher content of whey proteins cause problems making it difficult - in some cases impossible - to produce a cheese quality similar to the traditionally produced cheese.

Consequently, UF should not be considered as an alternative to traditional cheesemaking, but as a complementary process, adding value and benefits for cheesemakers and consumers alike. The general positive and negative effects of UF cheesemaking compared to traditional cheesemaking are illustrated in Table 23.

UF cheesemaking falls into a number of different categories as illustrated in Figure 95.

Pre-concentration. This is a concentration of the standardised cheese milk by a factor of two maximally. This can be used for most cheese types and is followed by the traditional cheesemaking procedure. If the volume is reduced to half of the original volume, the pre-concentration makes it possible to utilise the cheese vats and whey draining equipment better. At the same time the protein content is standardised with the benefits above described as a consequence.

Pre-concentration will not have any significant influence on the final cheese quality, since only a small amount of whey proteins will be included in the cheese. This, however, also means that there is no substantial increase in yield.

Figure 95: A comparison between traditional cheesemaking and a number of UF-based cheesemaking principles.

Strategy / Cheese type	Traditional technology (examples)	Protein standardisation pre-concent. up to 2 times	Part concentration 3-5 times	Full concentration normal PH	Full concentration acid curd pH approx 4.5	UF concentration + evaporation
Fresh cheeses	Quarg Cream cheese Cottage cheese Ricotta	Cottage cheese		Ricotta	Quarg Cream cheese Fromage frais	
Mould-ripened cheeses	Camenbert Brie Blue cheese Blue & white	Camenbert Brie	Blue cheese Blue & white Camenbert Brie			
Semi-hard cheeses	Tilsit, Havarti Gouda, Danbo, Feta, structured white cheese	Tilsit, Havarti Gouda, Danbo, Feta, structured white cheese	Tilsit, Havarti Gouda, Danbo, Feta, structured white cheese	Feta Quartirolo Yellow cast cheese		
Hard cheeses	Cheddar	Cheddar	Cheddar			
Raw material for re-processing				Cheese base		Cheese base

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	Cheese base

Positive	'Negative'
• Improved yield - whey proteins in the cheese • Continuous process • Closed system - good bacteriological control • Easy control of parameters and composition • New cheese types easily obtainable • High nutritional value - whey proteins in the cheese • Reduced rennet consumption	• Slower ripening • Poor meltability • Generally softer consistency • Controlled eye-formation difficult – all negative effects are because of whey in the cheese

Table 23: UF cheeses. General positive and 'negative' aspects compared with traditional cheeses.

Part-concentration. If the standardised cheese milk is concentrated 3-5 times, the subsequent cheesemaking procedure is modified. The batch cheesemaking vats are replaced with a coagulation system which works in a continuous mode. The concentrated milk is filled into coagulation tubes and mixed with rennet and possibly culture. After coagulation, the curd is cut into cheese grains of the required size, after which it is ready for dosing into moulds. Moulding, pressing (if required), and salting take place in the traditional way, and with traditional cheese equipment. This process is used for Queso Fresco, structured Feta, the traditional European cheese types, together with cheese types like Blue cheese, Camembert and Brie.

Depending on the cheese types and the efficiency of the traditional process, UF may increase the yield by as much as 10-15%.

Full concentration. If the standardised milk is concentrated to the final solids content in the cheese, all whey proteins will be included in the final product, and this gives the maximum yield increase without any whey drainage. This process is used for cheeses like cast Feta, quarg, Cream cheese, Ricotta and Mascarpone. If the concentration is combined with a final evaporation stage, the process can be used for the manufacture of Cheese base.

A special development is the so-called yellow cast cheese, where a ripened yellow cheese is produced directly from the concentrated milk without any whey drainage.

Feta cheese. The production of Feta cheese is one of the most successful applications of membranes in the dairy industry. It was initiated in the early 1970s by the private Danish dairy *Ørum Sogns Mejeri* in cooperation with APV.

By using UF to concentrate whole milk to 36-38% total solids in the concentrate, and then adding starter culture, rennet and salt directly to the concentrate, Feta cheese could be cast directly in tins as the final packaging material. The product was called cast Feta and it became an

almost instant success, partly because the production method was extremely simple, and partly because it entailed an increase in yield of more than 20%. This meant that the payback period for the investment in the processing equipment became very short indeed.

During the subsequent 5-10 years, all Feta-producing dairies in Denmark changed over to the UF process, and Feta became Denmark's most important export cheese. Since then, several other countries have entered the market for UF-based Feta production. Figure 96 illustrates the manufacture of cast Feta.

Fresh cultured cheese. This term is used as a common denominator for products like quarg, quarg desserts, Fromage frais, Pâte Fraîche and Cream cheese. Prior to the development of the UF process, these products were manufactured by means of specially designed centrifugal separators, sometimes combined with a special heat treatment of the feed. The UF process was originally based on concentration of fresh or slightly pre-ripened milk or cream with subsequent culturing of the concentrate, or through recovery of whey proteins from the acid whey, followed by re-dosing of the concentrated whey proteins into the cheese.

A real break-through came with the process illustrated in Figure 97. The milk or cream is cultured to a final pH of 4.5-4.6 followed by UF. Due to the extremely high viscosity caused by the low pH, the UF plant is based on a plate-and-frame type system, with a specially designed plate (module 37). The last loops in the plant are equipped with a positive booster pump in order to handle the highly viscous concentrate. This UF process makes it possible to manufacture products with exactly the required flavour and consistency. The yield increase is the highest of all known processes, and it is even possible to base the process on recombined or reconstituted milk from skimmilk powder and butter oil.

Figure 98 illustrates the design of a UF-based plant for production of fresh cultured cheese products. This process has been very successful, and many of these products are now produced by means of UF all over the world.

Ricotta originates from Italy where it is usually made from whey from a primary cheese production. Today, Ricotta is also produced from whole milk, skimmilk, whey, or a mixture of these. Traditionally, Ricotta is made from cultured milk and/or whey, followed by heating until the solids - mostly proteins and fat - precipitate and float. The cheese is then skimmed off, drained, and cooled prior

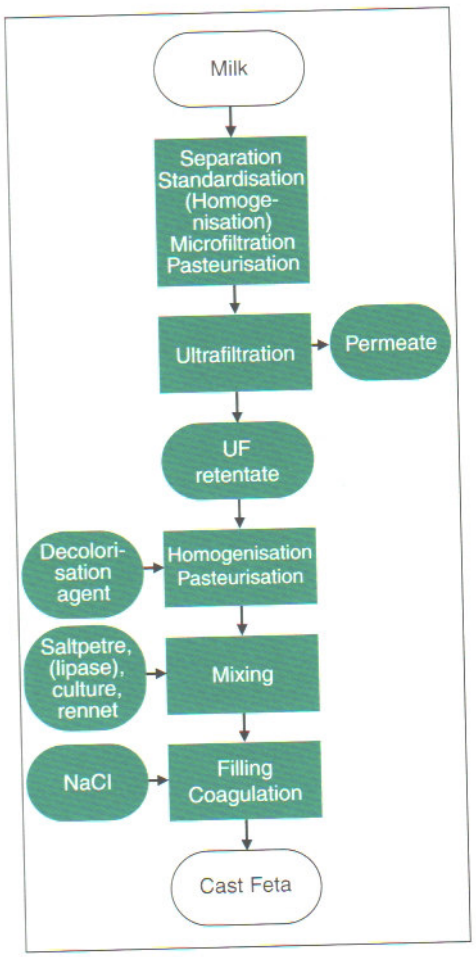

Figure 96: Manufacture of cast Feta by means of UF has become one of the most successful applications of membrane filtration in the dairy industry.

to packaging. This method has a number of disadvantages. The energy consumption is very high, there is a considerable amount of manual work involved, and the fact that the process takes place in an open system entails a risk of infection, especially by yeasts and moulds, which reduces the shelf life to 2-3 weeks.

The UF process for Ricotta is illustrated in Figure 99. Following a high-temperature pasteurisation, the mixture of milk and whey is concentrated to approximately 30% total solids in the UF plant. After addition of NaCl, the concentrate is heated to 90°C followed by in-line addition of lactic acid under pressure in a specially designed Ricotta unit. By means of an APV-patented back-pressure regulator, the pressure is reduced to atmospheric pressure, and this abrupt pressure drop causes the characteristic Ricotta grains to form. The mixture of grains and liquid is cooled to approx. 70°C followed by filling into airtight containers, which then undergo a secondary cooling to below 10°C in an ordinary cold store.

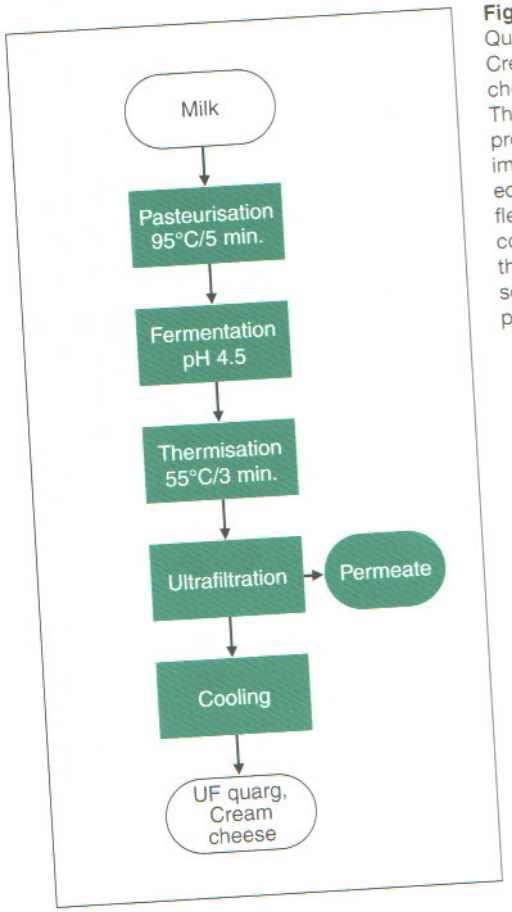

Figure 97: Quarg and Cream cheese. The UF-based process offers improved economy and flexibility compared with the traditional separator processes.

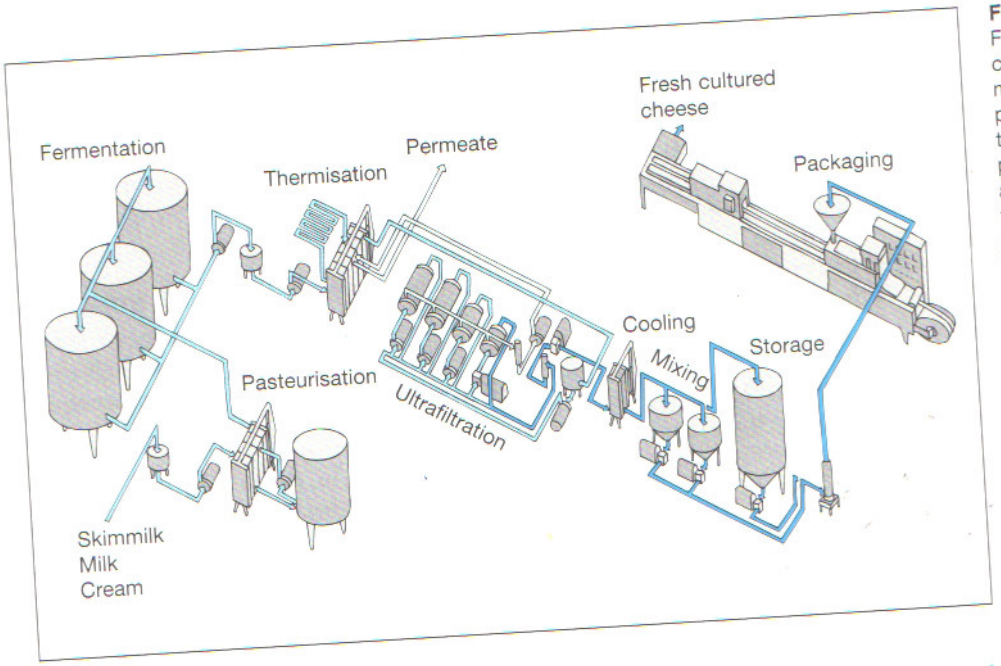

Figure 98: Fresh cultured cheese. The manufacturing process from the initial pasteurisation and fermentation of the milk, through UF and homogenisation, to cooling, mixing, final cooling, and packaging.

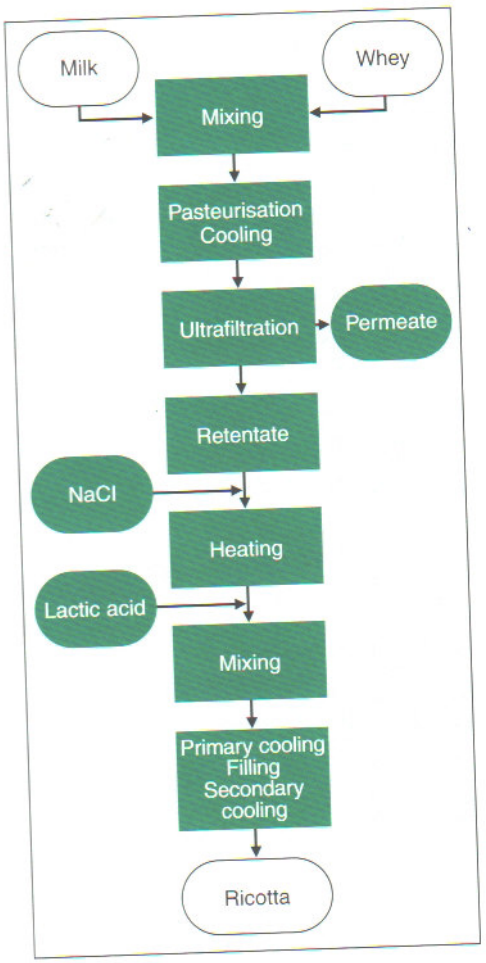

Figure 99: Ricotta. The UF Ricotta process requires less energy and provides excellent product quality compared with the conventional manufacturing process.

The process consumes much less energy and takes place in an entirely closed system, which eliminates the risk of infection and results in a product with excellent keeping quality. The continuous process reduces the manual handling to a minimum and thus provides for very rational production.

Cheese base is another successful application of UF-based cheese processing. In this case, whole milk is concentrated to approx. 38% total solids. Starter culture and rennet are added, and after culturing and renneting, the concentrate is further concentrated to 58-62% total solids by means of a swept (or scraped) surface evaporator. Finally, the Cheese base is drawn off from the bottom of the evaporator and cast into cheese blocks. The final product is used either directly as sliced cheese, or in the formulation of processed cheese. This is a greatly simplified process compared with the traditional Cheddar process, and the yield is increased by 15-20%.

Yellow cast cheese. Many attempts have been made to produce a ripened, yellow cheese based on a concentrate from UF of milk. This would eliminate whey drainage and render traditional cheesemaking equipment like vats and presses superfluous. Furthermore, it would increase the yield by as much as 20%.

During the late 1980s, APV developed a process in which the UF concentrate is in-line pasteurised in a scraped surface heat exchanger and cooled to fermentation and renneting temperature. Starter, rennet, and possibly ripening enzymes are also added in-line. Immediately after in-line mixing, the concentrate is led to a specially constructed, continuous mould filling system. After renneting, the cheese is stored for a few hours prior to de-moulding and storage on shelves for up to 15 hours. During this period, the fermentation to a pH of 5.2 takes place. The cheese is brined and ripened as in conventional cheesemaking. This produces a semi-hard, ripened cheese with a good quality and consistency, and optimises the cheese yield.

Whey/permeate treatment

In most cases, whey and permeate are used for further processing and this normally requires some form of concentration and - sometimes - demineralisation.

Concentration. In the early days of membrane filtration, RO was an important process for whey concentration. But concurrently with the improved performance and efficiency of evaporators, RO as a process for full concentration of

whey has become less important. However, for concentration of whey up to approx. 15-18% solids, RO is still very competitive.

The maximum obtainable concentration of whey depends on the type of whey, the processing temperature, the pre-treatment of the feed, fouling, etc. Table 24 illustrates the composition of various types of whey together with the osmotic pressure and the maximum obtainable concentration.

The BOD load of condensate from evaporators and permeate from RO plants is often too high for discharge directly through the sewer system. By means of an RO 'polisher', the BOD level can be reduced considerably, usually by a factor of ten, and the water may be used for cleaning purposes or discharged directly to the sewer.

Provided the permeate from the polisher is handled properly, or pasteurised or treated with UV light, it may be taken back for direct use as process water. The polisher is a low cost RO plant, based on spiral-wound elements normally in a fibre glass housing.

Demineralisation. By using NF membranes, it is possible to concentrate and demineralise the whey at the same time. This process has become quite popular in recent years as a way to improve the quality of the whey. The maximum level of demineralisation with NF is in the order of 30-35% reduction of the ash content. By using diafiltration, the level of demineralisation can be increased to 40-42% or even higher. Since whey and permeate in most instances have to pass through a concentration stage prior to further processing, the NF option becomes very attractive because the demineralisation is obtained without further cost.

Lactose manufacturing. Lactose is produced from whey or permeate, and membrane filtration plays a major role in a modern lactose factory. Figure 100 illustrates how lactose is produced from whey. The permeate from whey is concentrated to 60-70% total solids through RO followed by evaporation. The con-

Table 24: Composition of different types of whey.

	Sweet whey		Acid whey	
	Rennet cheese whey %	Rennet casein whey %	Lactic acid whey %	HCl whey/ H_2SO_4 whey %
True protein	0.60	0.60	0.60	0.60
NPN	0.20	0.19	0.20	0.20
Lactose	4.49	4.62	3.62	4.59
Fat	0.06	0.03	0.06	0.04
Acid	0.15	0.19	0.85	0.15
Ash	0.50	0.49	0.67	0.80
Total solids	6.00	6.12	6.00	6.38
Osmotic pressure (bar)	7.9	7.9	10.3	10.0
Max. concentration*	23	23	18	18

* Total solids obtainable by RO concentration when reasonable investments and operating costs are considered

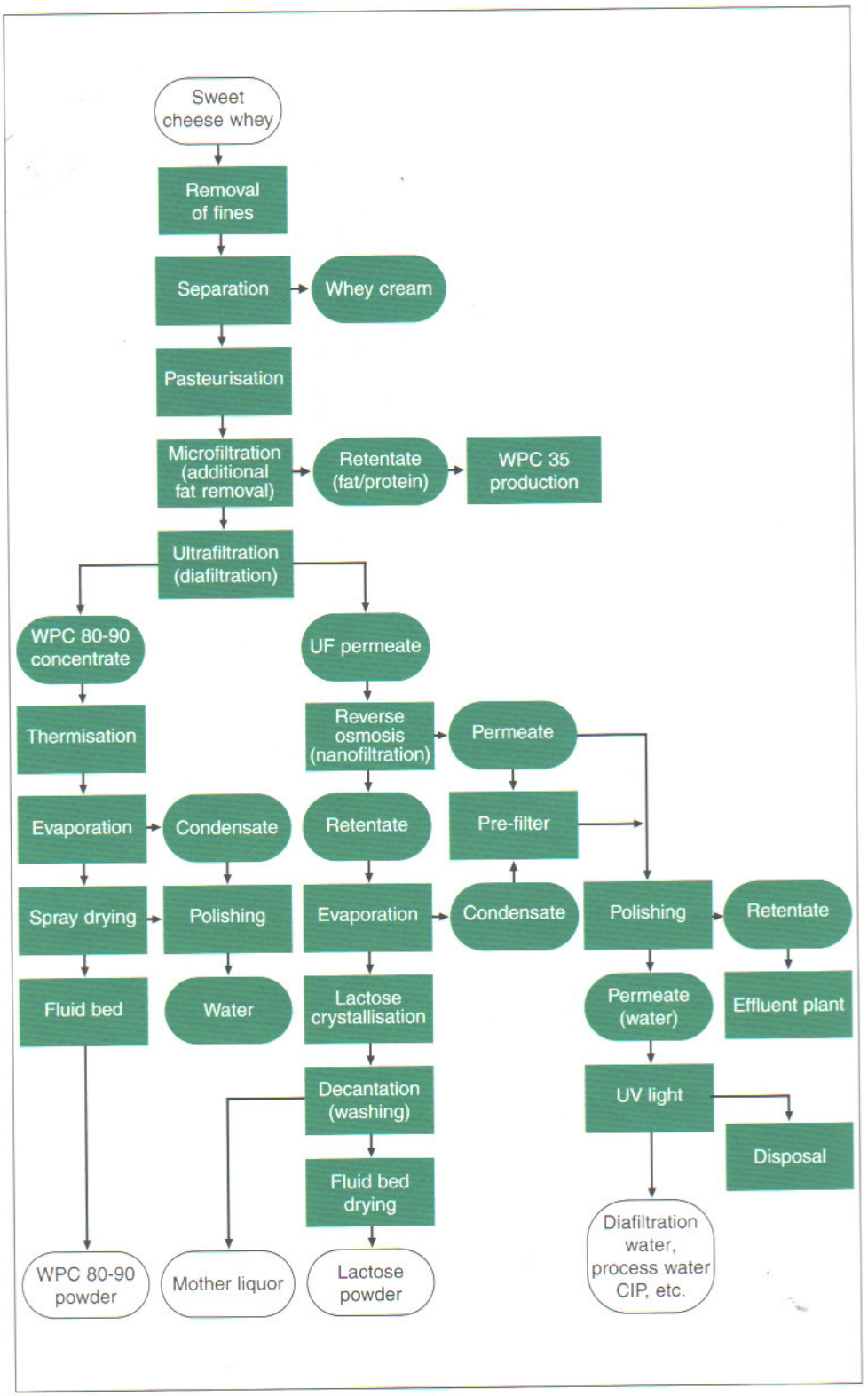

Figure 100: Process diagram for production of WPC and lactose. Membrane filtration is the key to manufacturing high value-added components. This has converted whey from a waste product into a valuable raw material.

centrated solution is fed to crystallisation tanks, where it is cooled and seeded to supersaturation. This initiates the crystallisation of lactose and subsequent growth of the crystals. Depending on the composition of the permeate, it may be necessary to precipitate calcium phosphate by increasing pH with sodium hydroxide, in order to avoid excessive scaling in the evaporator. After the crystallisation process is complete, the lactose crystals are separated from the remaining liquid - the mother liquor - by means of a centrifuge. The crystals are washed and then transferred to a stationary fluid bed lactose dryer.

Bacteria and spore removal

MF is used to remove micro-organisms such as bacteria and spores, together with impurities from milk, whey and cheese brine.

Figure 101 illustrates an MF process patented by APV. Following separation of the cream, the skimmilk is treated in the MF plant, and the bacteria-rich concentrate is led back to the inlet of the separator, where the bacteria and spores are discharged via the normal desludging procedure. The content of bacteria and spores in the sludge is considerably higher than in a system without MF concentrate feed-back. However, the volume of sludge is virtually unchanged and consequently, the APV process has no increased losses. Furthermore, the milk proteins are not affected by heat to the same extent as for alternative processes. The cream is subjected to a conventional high-heat treatment prior to being mixed back into the MF permeate, in proportion to the desired protein/fat ratio in the final product.

Contrary to traditional procedures, this process not only curbs the activity of bacteria; it physically removes bacteria, spores, dead cells and other impurities from the milk altogether.

Market milk. The MF process is used increasingly for treatment of market milk. The objective is to produce a value added milk with a higher purity and longer shelf life compared to milk treated by conventional heat treatment pro-

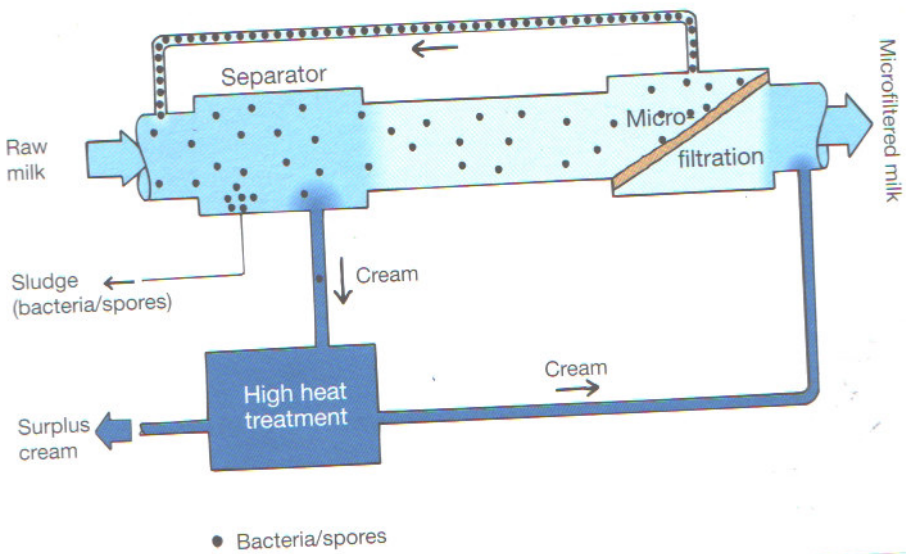

Figure 101: Removal of bacteria and spores from milk. Microfiltration is a key process in providing high quality milk for manufacture of cheese, powder, and consumer milk.

cesses. The product has been well received in the market place.

Cheese milk. Traditionally, the natural content of anaerobic spores like *clostridia*, which survive a normal pasteurisation, has been controlled by addition of nitrate and other additives. The nitrate prevents the anaerobic spores from developing and producing gas, which destroys or damages the cheese seriously. As a result of the consumer demand for fresh and natural products without preservatives, many markets now reject cheese which has been produced with addition of nitrate. MF eliminates the need for nitrate addition, and thereby allows access to wider and more lucrative markets.

Milk and whey powders. For production of various types of special powders, MF can be used to remove bacteria, spores and impurities, to give an exceptionally high powder quality. In production of WPC powders, MF is used for removal of a substantial part of the fat content left after separation, together with bacteria and spores, thus giving a very high quality powder exposed to only a minimum heat treatment, which contributes to the preservation of the functional properties of the whey proteins.

Cheese brine. The chemical and microbiological quality of brine used for salting cheese is critical for the production of high quality cheese. The brine may contain unwanted micro-organisms such as pathogenic bacteria, yeasts, and moulds. Traditionally, cheese brine has been subjected to different types of treatment, such as heat treatment, kieselguhr filtration, UV radiation and addition of preservatives. The most successful methods so far have probably been heat treatment and kieselguhr filtration, but both have limitations. MF is seen as the ideal process for sanitation of cheese brine, because it is fairly simple to perform, it does not destroy the balance in the composition of the brine, it does not produce large quantities of waste material, and it is reasonable in terms of maintenance costs.

The composition and quality of cheese brine vary widely from factory to factory, and this makes it difficult to give detailed performance data of general validity. Table 25 gives a summary of the experience with a number of different brine systems, and it shows that the criteria for purification of brine can be satisfied with MF.

The systems used have been based primarily on ceramic MF membranes, but recent developments with spiral-wound membrane systems offer additional advantages.

The concentrate volume typically makes up 0.5-1% of the feed volume and can even be regulated to as little as 0.3%.

Table 25: General facts on MF of cheese brine.

- Practically 100% retention of yeasts and moulds
- Very high retention of bacteria (>99.4% total count)
- Spores and thermophilic bacteria are removed
- Dead cells are removed, consequently there is no undesired enzymatic activity
- The chemical balance of brine is maintained along with very low retention of Ca and N
- No heat treatment therefore no change in pH (heat treatment causes pH drop of 0.2-0.4)
- Minimal chemical change (heat treatment causes precipitation of calcium phosphate)
- No denaturation of proteins (heat treatment causes 25-40% precipitation of whey protein)
- No filter aids required
- Continuous operation

Protein	% of total protein	Tertiary structure	MW	Size nm
• Casein	80	Micelles	400,000-2,000,000	50-300
• Whey proteins	20			
– α-lactalbumin	4	Globular	14,000	3-6
– β-lactoglobulin	10	Globular	18,000	3-6
– immunoglobulin	2	Globular	150,000-900,000	5-10
– blood serum albumin	1	Globular	66,000	3-6

Table 26: Configuration and size distribution of milk proteins.

The concentrate can be discharged or collected as waste. Normally the concentrate is regulated to correspond to the amount of surplus brine arising from the whey release from the cheese. The operating temperature is normally the same as that used for brining the cheese.

It should be noticed that when MF is exposed to a 'dirty' brine, it takes from 2-3 weeks to 1-2 months to bring the brine 'in balance' and re-establish stable operating conditions in the MF plant.

Milk protein fractionation

As the quality and reliability of membranes have improved over recent years and new membranes with pore sizes relevant for fractionation of proteins have been developed, milk protein fractionation is now becoming accepted as an industrial process.

The size of different proteins in milk is shown in Table 26. The difference in size between the whey proteins and casein makes it possible to use membranes for fractionation of casein and whey proteins, whereas further isolation of the individual casein and whey proteins has to be done by other technologies, such as liquid chromatography.

The purpose of fractionating milk proteins is to be able to standardise the concentration of casein, e.g. in relation to cheesemaking, manufacture of casein, or special casein-rich milk powders. This improves the cheesemaking procedure, and also gives a very good raw material for producing high quality WPI, since the MF permeate containing the whey proteins is free of fat, caseins, bacteria and spores. Furthermore, the whey proteins are present in the permeate in their natural form, unaffected by heat or enzymes from rennet or starter culture.

Figure 102 illustrates a mass balance for protein fractionation of skimmilk, showing the split into standardised skimmilk which can be used for processing high quality cheese, and a whey fraction which can be further processed into WPI and lactose.

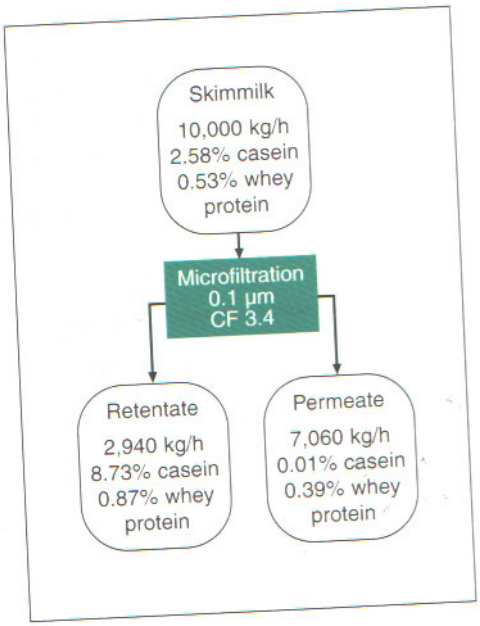

Figure 102: Microfiltration enables fractionation of milk proteins. This opens up for new methods for both cheese and casein manufacturing.

The fractionation and standardisation of milk proteins opens up new ways of manufacturing cheese and casein.

Fermented and alcoholic beverages

The industries producing fermented and alcoholic beverages increasingly apply membrane filtration technologies in different areas. So far, the applications have not been able to match the success experienced by the dairy industry, but there is ample reason to believe that this will change in the future.

Also the production of vinegar from diluted alcohol solutions has benefited considerably from using UF or MF for clarification of the fermented solution, replacing conventional and more labour intensive clarification techniques.

Beer

Figure 103 shows a general flow sheet of beer brewing with indications of where membrane filtration can play a role.

The most successful application so far has probably been recovery of beer from surplus yeast, and filtration of return and residual beer. In the future, filtration of main stream beer may become the most important application, provided the technology can be developed to fully substitute the conventional technology for beer clarification.

Low-alcohol beer. Consumers are becoming increasingly health conscious, and the concern about driving under the influence of alcohol is increasing in most countries. This has raised the interest for beer with a low alcohol content, without impairing its taste and other characteristics.

The most simple way to remove alcohol from beer is through vacuum evaporation, but this process also removes components which help give taste and texture to the beer.

By means of dialysis (see Chapter 3), alcohol is removed at cellar temperature without seriously affecting the product quality in terms of head retention, colour, taste or shelf life. The alcohol content can be varied from 4.2% to 0.5% v/v.

A third way is to use RO in combination with diafiltration, where the alcohol, so to speak, is washed out of the beer. This provides an excellent quality beer and maximises the retention of flavour.

Beer recovery from surplus yeast and tank bottoms. During the production of beer, roughly 1.5 to 2% of the total beer output from the fermentation and storage processes is composed of a mixture of yeast and beer (Figure 103). Up to 50% of this valuable beer content can be recovered from the surplus yeast and tank bottoms, by a suitable process. The yeast represents roughly 1.5 l/hl beer, while the tank bottoms are about 0.5 l/hl beer. The mixture of yeast and beer from the fermentation and conditioning consists of about 40% yeast cells and 60% beer v/v. The beer fluid clings to the yeast and cannot be separated without special measures. This beer is lost to the brewery if the yeast is sold or otherwise disposed of.

Decanters and centrifuges can recover up to 50% of the beer. However this is usually associated with a fairly high oxygen take-up, and a large number of yeast cells are destroyed by the shear forces in disc stack centrifuges. As a result, the cell fluids are released to the beer and degrade the flavour. This also reduces the foam stability of the recovered beer and only small fractions can be blended back to the main stream beer without significantly impairing the quality.

Another method is to use yeast presses working at pressures up to 15 bar which can recover up to 60% of the beer. How-

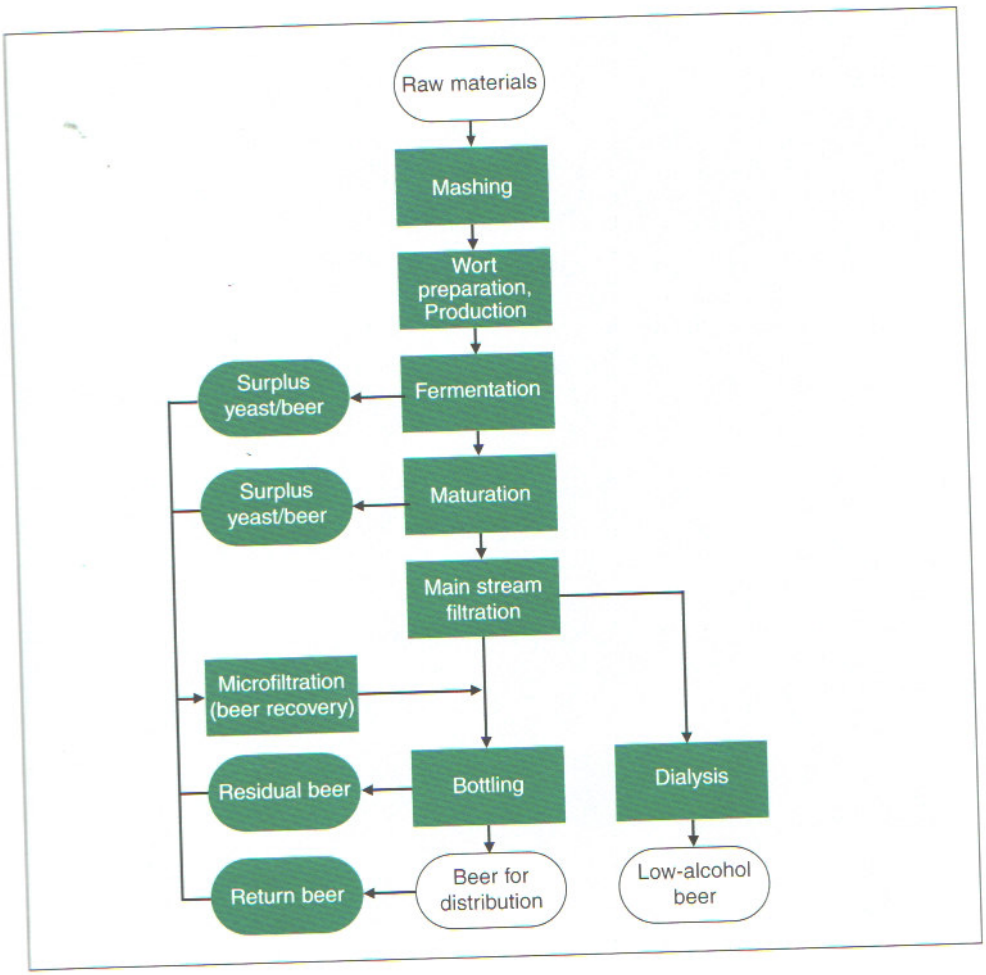

Figure 103: There are three main applications for membranes in the brewing industry: beer recovery, low-alcohol beer, and main stream beer clarification.

ever, the high pressure also results in destruction of yeast cells and consequently the recovered beer has an increased pH value, a bitter flavour and a different colour. This beer can only be returned to the brewhouse or fermentation cellar for further processing.

MF offers an ideal alternative to these methods. By using ceramic membranes with a pore size of 0.5 µm (alternatively 0.8 µm), it is possible to obtain a quality of the filtered beer which is very close to the quality of normal bright beer.

Even though beer is a fairly uniform product around the world, the brewing methods vary in terms of raw materials, original gravity, fining agents, etc. This may influence the specific capacity of the MF plant, and in some cases it may be necessary to carry out pilot tests on site, prior to dimensioning a full scale plant. The capacity is usually in the order of 20-50 lmh depending on the product treated and the method of fermentation.

The recovered beer is clear and almost sterile with practically no micro-organisms present, and consequently it is possible to blend the recovered beer back into the high-value main stream beer. The yeast concentrate recovered usually contains up to 20-22% total solids, and it can be sold as animal feed or otherwise disposed of.

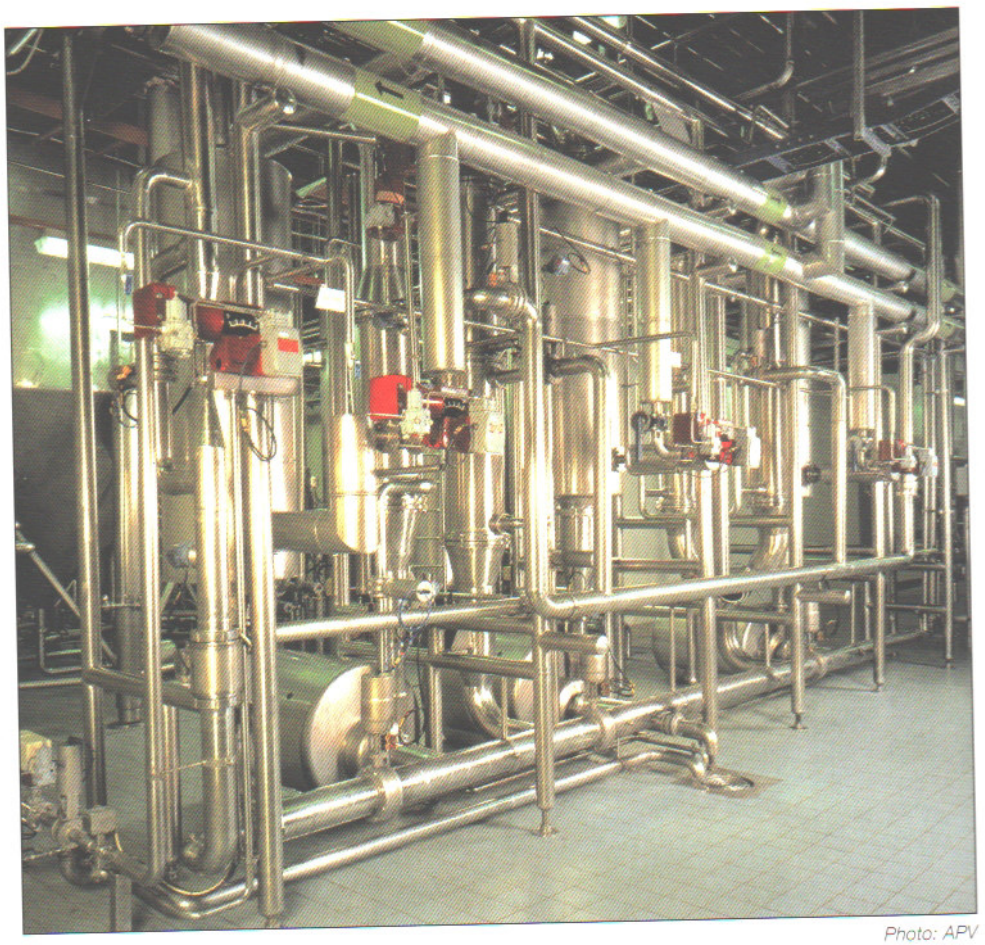

Photo: APV

Figure 104: Microfiltration plant for beer recovery from surplus yeast.

As a general rule, this technology increases the yield by approximately 1% of the total beer production. Figure 104 shows an MF beer recovery plant in a brewery.

Main stream beer filtration. In the traditional pasteurisation process, the thermal load may adversely affect organoleptic qualities attributed to organic flavour producing compounds.

To ensure satisfactory bacteriological quality prior to bottling, bacteria removal using microfiltration is being evaluated as an alternative to the traditional beer pasteurisation process.

Approximately 85% of all beer produced around the world is currently clarified using filtration of some sort but MF may eventually replace conventional filtration and pasteurisation of beer. Provided MF can be successfully scaled up to an industrial process, this would become a very large area for membranes. The key to this is to find a membrane with the correct characteristics enabling retention of all micro-organisms, yeast cells and haze, allowing full permeability of all the components giving beer its colour, flavour, texture, etc. This would also solve the increasing problems the brewing industry has in terms of disposal of kieselguhr, since MF basically would eliminate the need to use conventional filters and filter aids.

Photo: APV

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Wine

Membrane filtration is also playing an increasing role in the wine industry. Primarily for wine clarification and because of its ability to remove yeasts and bacteria cells. This should contribute to a reduction of the use of additives such as SO_2 or ascorbic acid. The use of both MF and UF in wine making should, furthermore, reduce the number of processing steps, such as racking, centrifugation, kieselguhr filtration, and cartridge filtration, either partially or totally.

Figure 105 shows the processing steps in conventional wine making. This includes a number of clarification/filtration stages:

(1) Clarification and biological stabilisation of musts
(2) Centrifugation after first racking of young wine
(3) Diatomaceous earth filtration after first racking of young wine
(4) Pre-filtration with depth filters
(5) Clarification and biological stabilisation of unprocessed wine by conventional dead-end filtration

The considerable variations in filtration characteristics of wines are typically the result of complex mixtures of suspended and colloidal matter, present in natural grape juice. Additional variations occur during the alcoholic and malo-lactic fermentation, as well as during the fining.

Various colloidal and non-colloidal particles are typically found in most wines as listed in Table 27. They originate from the grapes, fermenting yeast, bacteria and moulds. A knowledge of the wine composition is important, since it is often decisive for the degree of clarification needed.

MF, or sometimes UF, membranes are generally very effective in removing colloidal particles, but they are also sensitive to fouling. This makes the pre-treatment of the wine prior to the membrane system essential, and sometimes car-

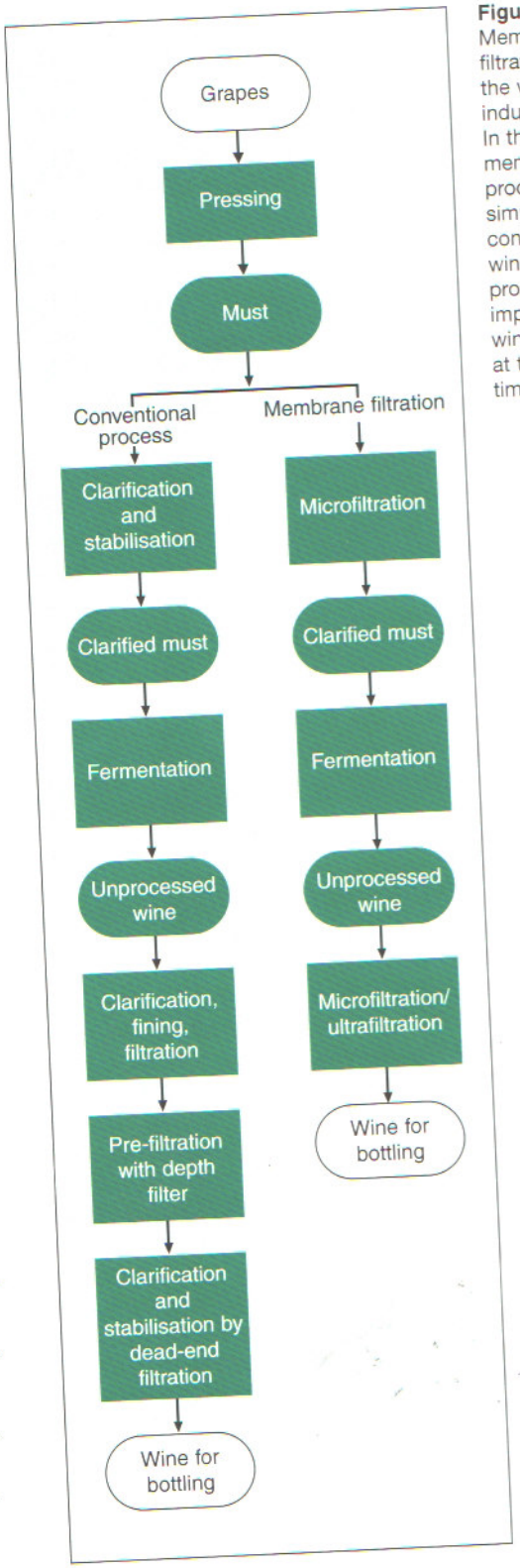


Figure 105: Membrane filtration in the wine industry. In the future, membrane processes may simplify the conventional wine making process and improve the wine quality at the same time.

Table 27: Typical particles and components in wine.

Particle size µm	Particle description
0.01-0.1	Peptides
	Proteins
	Polysaccharides
	Gums
	Dextrins
	Pectins
	Condensed tannins
	Leucocyanins/anthocyanins
	Phenolic compounds
0.5-1.0	Tartrate crystals
1.0-3.0	Yeasts (*Saccharomyces* sp., *Hensenula, Turolopsis, Debaromyces, Candida, Kluyveromyces, Pichia* and *Brettanomyces*
0.5-7.0	Bacteria (*Leuconostoc, Acetobacter,* etc.)
50-100	Diatomaceous earth, fibres and debris)

tridge depth filters are placed ahead of membrane filters in order to get the optimum solution.

Experience has proven that 0.1 or 0.2 µm MF membranes (Al_2O_3 membranes covered with a ZrO_2 active layer) are the most suitable membranes for wine filtration. Such membranes have excellent rejection characteristics for turbidity and micro-organisms, while still allowing permeation of polysaccharides, polyphenols, and alcohols essential for the organoleptic characteristics of the wine. The concentrate from the process usually constitutes only 1-2% of the total feed volume in the form of a semi-solid phase of rejected particles, yeast, bacteria, and a suspension of colloidal material.

During recent decades, the wine industry has witnessed a significant development in the process technology of wine making. Figure 105 indicates where MF/UF may play a role in this development, especially in the large European wine producing countries.

Vinegar

Vinegar is produced by fermentation of a diluted alcohol solution by means of the bacteria *acetobacter*. The fermented vinegar contains pectin, proteins, tannins, and metals such as iron, zinc and copper. The metals react with proteins and tannins and form colloids, which have to be removed in order to produce a sparklingly clear product. The reaction time, however, is 3 to 6 months for the colloids to form, somewhat depending on the raw materials. Traditionally, the colloids are removed through a fining process by means of bentonite filtration after 3 to 6 months' storage.

This fining process can be replaced by UF, which removes the high molecular weight substances, causing the formation of the colloids. The proces does not require the long storage period and is normally carried out batch-wise and, at the end, the concentrate is diafiltered in order to maximise the yield. This reduces the concentration of acetic acid, which is

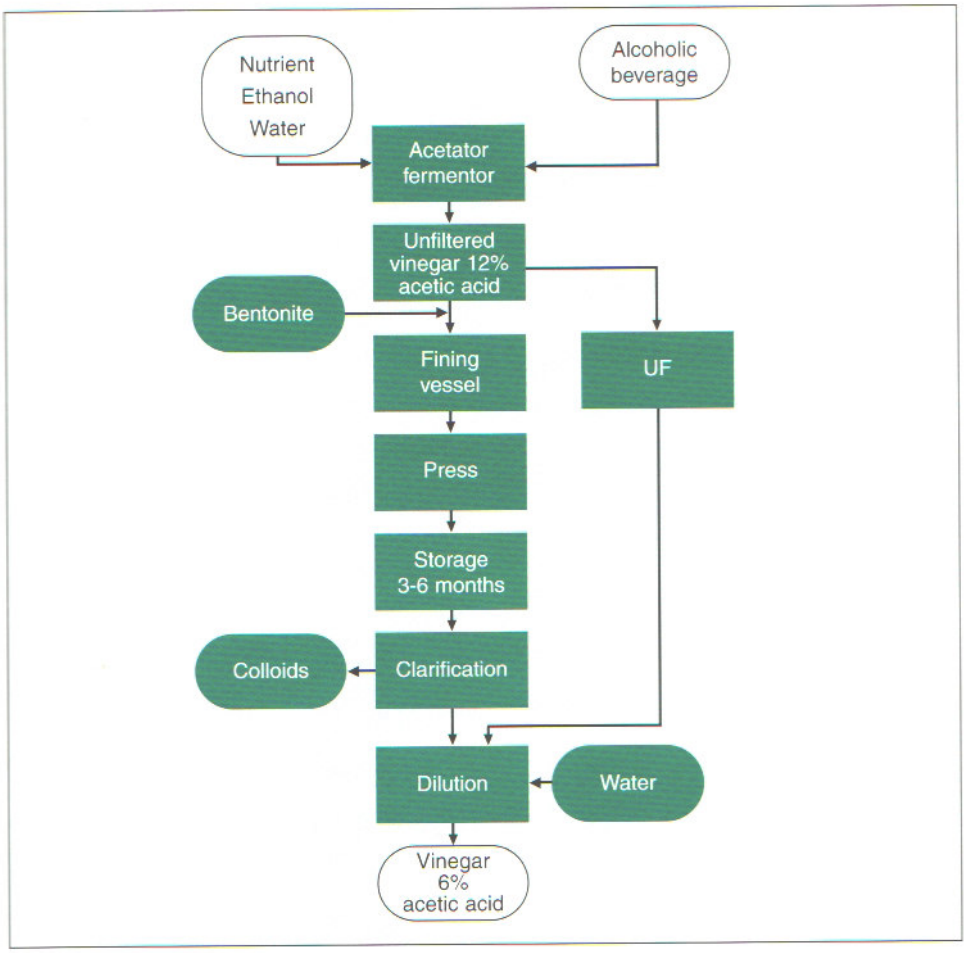


Figure 106: UF makes it possible to by-pass the conventional troublesome fining and clarification process and reduce the overall cost of vinegar manufacturing.

approximately 11-12% after fermentation. However, this is of minor significance, since the vinegar has to be diluted to 5-7% acetic acid anyway, which is the concentration in the final commercial product.

Figure 106 shows how UF can by-pass the traditional troublesome fining and clarification process in the production of vinegar.

Fruit juice

For several years, membranes have been applied in the fruit juice industry for clarification and concentration purposes.

The previous methods for juice clarification were both very time-consuming and labour-intensive. Furthermore, they required addition of large amounts of depectinisation and de-starching enzymes, bentonite, gelatine, and other chemicals and additives, which are costly and sometimes cause environmental disposal problems. The traditional fruit juice clarification process also requires investments in centrifuges, rotary vacuum filters for diatomaceous earth, pre-coating and cartridge polishing filters.

To a large extent, membrane filtration technology has made it possible to simplify the processes for clarification of fruit juices and simultaneously reduce

operating costs. In many cases, the quality of the final product has also been improved.

Most fruit juice is manufactured in areas far away from the consumers and, consequently, the juice has to transported over long distances before it reaches its final destination. In order to save on transportation costs, the juice is usually concentrated 6 or 7 times prior to transportation, and reconstituted close to the consumers.

This concentration is usually done by means of evaporators, specially designed for this purpose. However, the high temperature in the evaporator changes the quality of the juice and consequently RO has been tested as a way to remove the bulk of the water in a more gentle way, prior to the final concentration to 65-72°Bx in the evaporator.

Clarification

Clarification is used for different types of fruit juice but apple juice represents by far the largest volume being treated with membrane filtration. Figure 107 illustrates the various stages in apple juice production, both by the traditional method and by membrane filtration.

Raw juice is produced from chopped and milled apples by means of hydraulic presses, belt presses, and, in some instances, decanters. Sometimes, the fruit may undergo an enzymatic pre-treatment in order to assist the extraction of juice. The enzymes reduce the level of pectins contained in the cell walls.

Single strength juice is juice obtained from the first pressing. Juices for concentrates are usually obtained by pressing the mash twice. The juice is normally pasteurised in order to deactivate undesirable enzymes and micro-organisms.

Apple juice from a press or an extractor contains not only discrete particles but also unstable compounds which coagulate by the influence of heat or enzymes. Depending on the pressing or extraction conditions, the amount of spin solids in the fruit juice varies from 0.5 to 5%.

Clear juice is produced by separating the liquid phase from the insoluble substances while cloudy and pulpy juices, on the other hand, contain insoluble solid particles.

For the production of clear fruit juice, different filtering aids have traditionally been used. Most commonly, diatomaceous earth in the form of kieselguhr has been used but this is creating increasing disposal problems. Also, the resulting juice clarity is not always satisfactory, due to haze formation which may occur during storage.

Haze and turbidity develop in apple juice due to aggregation of proteins, starch and tannin. Tannin - a polyphenolic compound - causes the complexes formed to turn dark brown in colour. Bentonite, gelatine, etc. are sometimes used to prevent haze and turbidity formation.

Membrane filtration eliminates some of these steps, reduces the consumption of additives and increases yield and quality. A summary of the differences appears in Table 28.

Membrane clarification plants are usually built as batch plants, primarily because the enzymatic process prior to the membrane system is carried out batch-wise.

Both organic and ceramic membranes are used, normally with pore sizes of 0.1-0.2 µm. Due to the high level of solids, tubular systems are most commonly used, either in the form of 3.65 m long ½-inch tubular membranes, or ceramics with 6 mm channels.

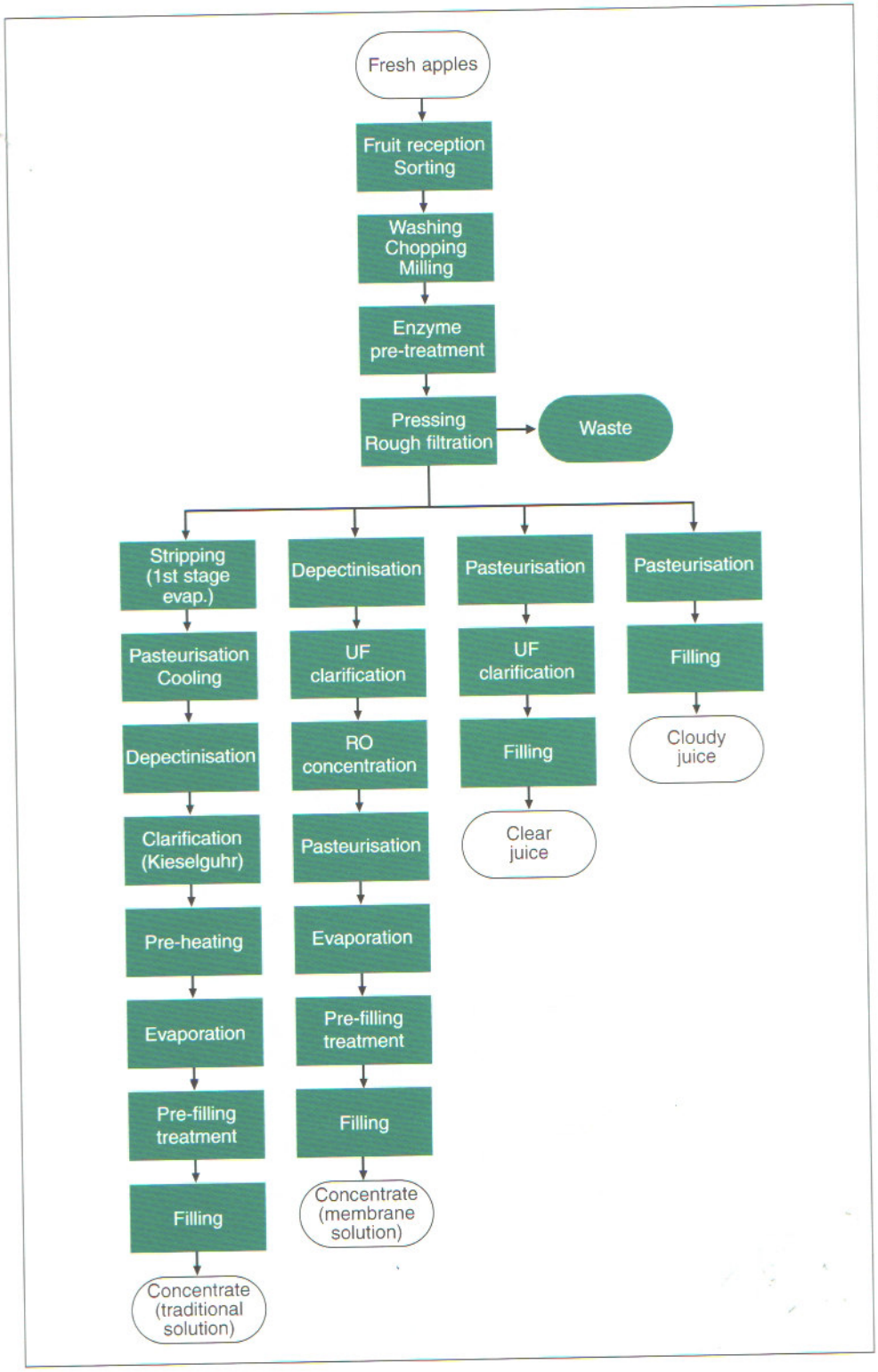


Figure 107: Apple juice clarification and concentration. Membrane filtration is widely used for apple juice clarification, as it reduces the processing costs and improves the quality at the same time.

Table 28: Comparison of parameters for clarification of fruit juices.

Parameter	Membrane filtration	Traditional method
Process step after pressing	Optional enzyme treatment, membrane filtration	Centrifuge, enzyme treatment, fining, polishing
Processing time after pressing	2-4 hours	12-36 hours
Yield	Minimum 95% (UF/MF + diafiltration: 99%)	Approximately 90%
Operating costs	1x	4-5x
Gelatine, bentonite, diatomaceous earth	Can be omitted	Required
NTU (apple)	<1	2.5

A process using inorganic membranes for bacteria removal as well as for clarification makes it possible to produce the final juice in one step. This process was launched under the name of Ultrapress™ by Carre Inc. - a subsidiary of DuPont Separations. The membranes are inorganic in nature, and deposited on a microporous metallic support. The membrane tubes are very wide (0.03 m) and the pressures applied are in the order of 15-20 bar.

The general process described for apple juice may also be applied for most other juices produced from cranberry, cherry, black currant, pear, peach and pineapple. In each case, pilot testing may be necessary in order to design a full scale plant.

Food industry

The food industry encompasses a large variety of different products and processes, and a complete review is beyond the scope of this book. Some of the most familiar and successful applications are, however, described in this section.

Egg processing

Eggs can be converted into liquid, frozen or dried products. Egg white is very sensitive to heat treatment, and this must be taken into consideration when eggs are processed into industrial products. Due to the high water content (88% in egg white), the conversion by spray drying into powder is very energy-consuming and costly. Therefore membrane filtration plays a natural role in the processing of eggs into concentrated and dried products.

Figure 108 is a flow sheet of egg processing on an industrial scale, and shows where membranes can be utilised. The composition of egg white, egg yolk and the corresponding dried products is shown in Table 29.

The pasteurisation of egg products prior to further processing must be executed with care since the proteins start to coagulate at 60-65°C. Therefore, pasteurisation temperatures usually have to be kept below 60°C, provided the proteins are stabilised by adjusting the pH to 7. The addition of small amounts of aluminium sulphate (only allowed in some countries) provides an extra stabilisation that enables pasteurisation at 62-64°C.

The egg proteins are also very sensitive to mechanical shear, which may destroy some of their functional properties like whipping ability, and cause the proteins to coagulate. This must be taken into consideration when choosing pumps, valves and other components.

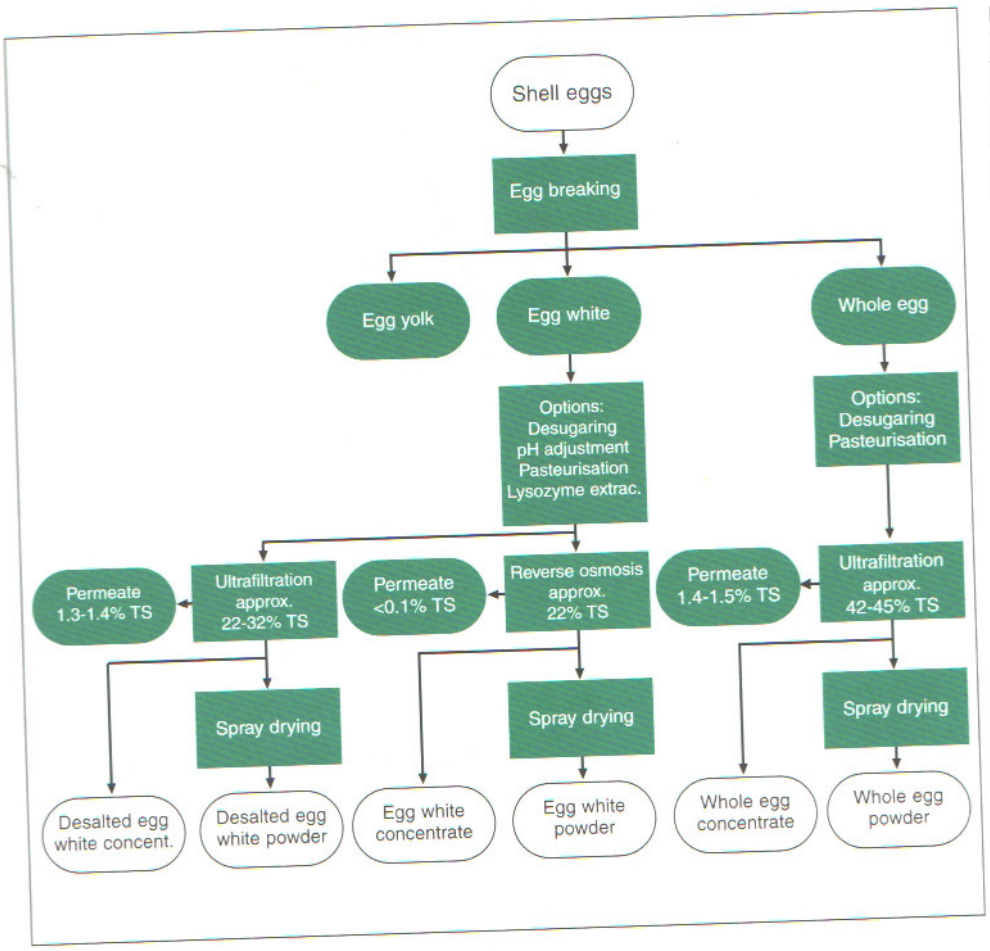


Figure 108: Membrane filtration is used for concentration and purification of egg white and whole egg.

Fresh egg		Whole egg	Egg white	Egg yolk
Total solids	%	25.0	12.0	51.0
Protein	%	12.0	10.5	17.5
Fat	%	11.0	0.03	32.5
Ash	%	1.0	1.0	1.0
pH		7.5	9.0	6.3
Dried egg		**Whole egg**	**Egg white**	**Egg yolk**
Total solids	% (min)	95.0-96.0	92.0	95.0-96.0
Protein	%	45.0	80.0	30.0
Fat	% (min)	40.0-45.0	-	56.0-63.0
Red sugar	% (max)	0.1	0.1	0.1
pH		6.5-7.5	6.5-7.5	6.0-6.6

Table 29: Composition of egg and dried egg products.

Table 30: Composition of blood and blood products.

		Blood	Blood plasma	Blood cell fraction
Total solids	%	18-20	9.2	33-35
Protein	%	13-15	7.9	33
Fat	%	0.4-0.8	<1	<1
Minerals	%	1.25*	1.5*	1
Carbohydrates	%	0.06-0.09		
Specific gravity	g/ml		1.028-1.032	1.080-1.105

* Most of the salts consist of citrate added as an anti-coagulant, usually 1% of a 40% sodium citrate solution

Glucose reduces the stability of manufactured egg products and is usually removed through an enzymatic pre-treatment process. By using UF membranes, the glucose content is automatically reduced, which contributes to improved product quality.

Egg white concentration. Egg white can be concentrated by RO from 12 to approximately 22% total solids prior to spray drying. If the egg white is concentrated by UF, it is possible to reach as much as 32% total solids. During UF, some of the glucose and ash content is removed in the permeate, which results in a value-added product in the form of a desalted egg white powder.

Whole egg concentration. Whole egg is more difficult to process due to the high fat content (11%). This makes CIP of the plant more difficult. For this reason, whole egg is concentrated by UF, only because the UF membranes can tolerate the chemicals necessary for proper cleaning, whereas RO membranes still are too sensitive for such harsh cleaning procedures. Commencing with a total solids content of 25%, it is possible to reach approximately 42% total solids in the concentrate.

Some of the original development in egg processing with membranes was based on the plate-and-frame system. Today, most egg white treatment plants are based on systems using spiral-wound elements. These systems have shown remarkably good results in terms of flux levels and their ability to be cleaned after each production. For whole egg processing, spiral-wound elements with 48 mill spacers give equivalent results to plate-and-frame systems. However, in the long term, the plate-and-frame system is preferred because it is easier to keep clean.

Blood processing

Blood has a very high nutritive value as a protein resource, and it is a valuable additive in the food industry because of the excellent functional properties of the blood proteins.

A mammal has a blood quantity of approximately 7.5% (w/w). During sticking, only 50-60% of the blood is collected, while the remainder stays in the body, e.g. in the organs, muscles, stomach, etc. On average, 13-16 litres of blood are collected from grown cattle and 2-3 litres from hogs. World-wide, 60% of processed blood comes from cattle, 30% from pigs and 10% from sheep. Table 30 illustrates the chemical composition of various blood products.

Blood consists of a blood plasma fraction (65%) and a cell/corpuscles fraction (35%). Blood plasma is the most valuable part of the blood. Most (85%) of the total solids in blood plasma is protein consisting of albumin, immunoglobulin, lipoprotein, transferrin, and fibrinogen.

Also, 75% of the proteins have a molecular weight higher than 70,000.

Blood has practically the same biological value as lean meat and it is an excellent source in the diet when combined with other proteins, e.g. caseinates. It also contains valuable minerals.

Figure 109 shows the complete diagram for blood processing, including the use of membrane filtration.

After the blood cell fraction has been removed from the plasma fraction by means of a separator, the plasma proteins are concentrated by UF from 7 to 26% protein. At the same time, citrates and salts are removed in the permeate. This results in a higher quality plasma protein than that obtained by conventional vacuum evaporation. In order to protect the membrane system against fouling, the plasma is pre-filtered, and anti-coagulants (citrate/phosphate) may be added.

Both spiral-wound and plate-and-frame systems are used. With the plate-and-frame system, it is possible to reach 30% total solids in the concentrate while the spiral-wound system can only provide up to 20% total solids in the concentrate. The concentrate is spray dried to a powder with a moisture content of 5%. The permeate, containing 1.5-2% total solids, may be further processed by means of RO.

Dried plasma has excellent functional properties and is used as a supplement or a substitute for meat protein, due to its good emulsifying and water binding characteristics. Plasma is used in luncheon meat, sausages, pâtés, soups, minced meat, etc. It is also used in different cereal products, due to the high content of the amino acid lysine, which complements the composition of the cereal proteins.

The blood cell fraction is further processed by removing the iron pigment from the haemoglobin, and isolating the proteins by treatment with acetone and enzymatic hydrolysis. The hydrolysed proteins may be concentrated by UF prior to spray drying.

Gums

Is the designation for a long line of products which are used as gelatination, thickening, and stabilising agents. Gums are classified under the following categories:

- Natural gums
- Modified natural gums
- Synthetic gums

Natural gums are for the greater part vegetable and plant extracts, with the exception of gelatine, which is of animal origin. Modified natural gums have been treated chemically or microbiologically. Synthetic gums are based mainly on products from the petrochemical industry.

Gums is chemically very different, but they have one thing in common - the ability to form gels. The concentration at which the gel is formed may vary considerably. Gum arabic is soluble up to 50% concentration, carregheenan forms a soft gel at 2% concentration, and agar forms a very firm gel already at 1% concentration. Due to this variation, chemically as well as physically, the gums are used in a range of different industries:

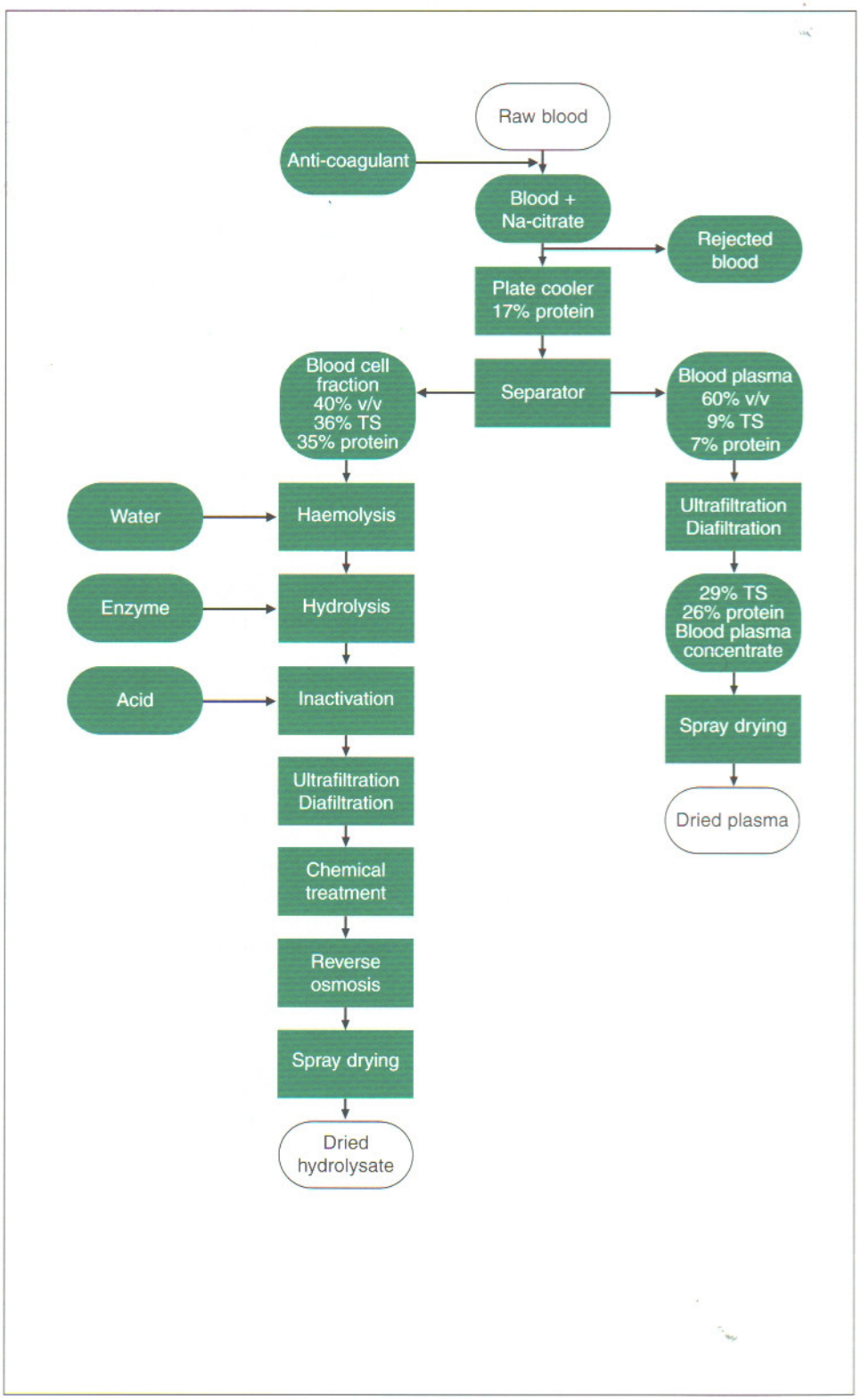
- The food industry
- The pharmaceutical industry
- The photographic industry
- The brewing industry

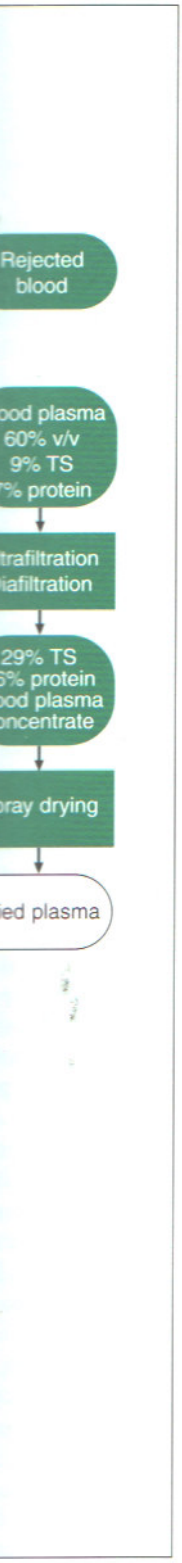
Table 31 shows the various categories and types of gums, while Table 32 shows some of the processed food applications.

Gelatine

Gelatine is manufactured from cattle

Figure 109: Using UF and diafiltration improve the quality of the final blood plasma or blood cell fraction.





hides, pig skins and bones, all of which contain the insoluble poly-peptide collagen. The raw materials are extracted at high temperatures with acid or alkali. The extract will typically contain 2-5% protein in the form of poly-peptides, in the molecular weight range from 15,000 to above 400,000. The extract also contains approximately 0.6% ash.

The extract needs to be clarified which traditionally is done by means of kieselguhr filters and cellulose sheet filters of 20 µm. MF is an alternative to the traditional clarification process. It will also remove the very high molecular weight fraction of the gelatine extract, and this results in a gelatine with improved functional and physical properties. Production of low ash gelatine, e.g. for photographic purposes, may, furthermore, require ion exchange.

Traditionally, the clarified gelatine solution has been concentrated by means of vacuum evaporators to 25-40% TS. However, the evaporation is liable to cause some product degradation and loss of physical properties. UF can take place

Natural gums	
Plant exudates	Arabic Tragacanth Karaya Ghatti
Seed or root	Locust bean gum Guar Psyllium seed
Seaweed extracts	Agar Alginates Carragheenan Furcelleran
Others	Pectin Gelatine Starch
Modified natural gums	
Cellulose derivates	CMC Methyl cellulose
Starch derivates	
Microbiological fermentation gums	Dextran
Synthetic gums	
Vinyl polymers Acrylic polymers Ethylene oxide polymers	

Table 31: Natural, modified natural and synthetic gums.

Functional property	Application
Adhesive	Bakery glaze
Binding agent	Sausages
Calorie control	Dietetic foods
Crystallisation inhibitor	Ice cream, sugar syrups
Clarifying agent	Beer, wine
Clouding agent	Fruit juice
Coating agent	Confectionary
Emulsifier	Salad dressings
Encapsulating agent	Powdered flavours
Film former	Sausage casings, protective coatings
Flocculating agent	Wine
Foam stabiliser	Whipped toppings, beer
Gelling agent	Puddings, desserts, aspics
Moulding	Gum drops, jelly candies
Protective colloid	Flavour emulsions
Suspending agent	Chocolate milk
Swelling agent	Processed meats
Syneresis inhibitor	Cheese, frozen foods
Thickening agent	Jams, pie fillings, sauces
Whipping agent	Topping, icings

Table 32: Functional properties of gums in processed food applications.

at a lower temperature (40-55°C) and has proven to be a very suitable replacement for the vacuum evaporators. Depending somewhat on the product quality, it is possible to concentrate the gelatine to 25% TS by means of UF. The membrane systems used for this concentration are normally of the spiral-wound type.

Following the concentration by UF, the gelatine is subjected to a flash sterilisation at 140°C. The sterilised solution is rapidly cooled and extruded in gel forms under aseptic conditions. The extruded gel passes through a continuous dryer (spray or roller dryer), and is finally ground into granules or powder.

Figure 110 shows a flow diagram for the production of gelatine using membrane filtration. The figure refers to type A gelatine based on acid processing, and type B gelatine based on alkaline or lime processing of the raw material. The further processing is identical for the two types, but the two products differ in their isoelectric point, which is pH 7-9 for type A and 4.8-5.2 for type B.

The final product ranges from coarse granules to fine powders and thin sheets. It contains 9-12% moisture and 85-90% protein, and is essentially tasteless, odourless, and brittle. Gelatine is widely used in the food industry, in the pharmaceutical industry, in the production of photographic films, and as a glue.

Pectin

Pectin is a poly-α-1.4-galacturonic acid, where part of the acid is esterified with methanol. This is a composition similar to the so-called hemi-cellulose, which is a main component in the composition of the cell walls of plants.

Pectin in the form of protopectin is found mainly in fruits and roots. By enzymatic reactions in the living organism, protopectin is converted into soluble pectin.

Pectin is used for its ability to increase viscosity and bind water. Typical applications are in production of gels, jams, and marmalade. Pectin is also used to increase turbidity or viscosity when added to juice or various tomato products.

The raw materials for the production of pectin are normally apple pomace and the 'white' of citrus fruits. Figure 111 shows a flow sheet for the production of pectin. UF is used after the extracted pectin has been clarified.

The pectin concentration in the extract is approximately 1%, and by means of UF it is possible to achieve a 5-7 times concentration by volume, corresponding to a concentration of 4-6% in the concentrate. During the UF process, low molecular weight substances like sugars are removed, which improves the quality of the final product.

Vegetable protein

Vegetable protein products are an important part of the basic diet in many developing countries. Besides being an important fodder in modern animal production, it is also used as a source of meat substitute.

The rapid development in Asia, the change in demographic conditions in many parts of the world, and last - but not least - the explosive growth in world population have increased the need for utilisation of vegetable protein.

The most commonly known vegetable protein source is the soy bean but there are other lesser known crops, such as the faba bean (able to grow under more temperate climatic conditions), which are also rich sources of protein.
Potatoes are also a source of vegetable protein. Membrane filtration is especially useful when handling the very large amounts of waste water from the production of potato starch.

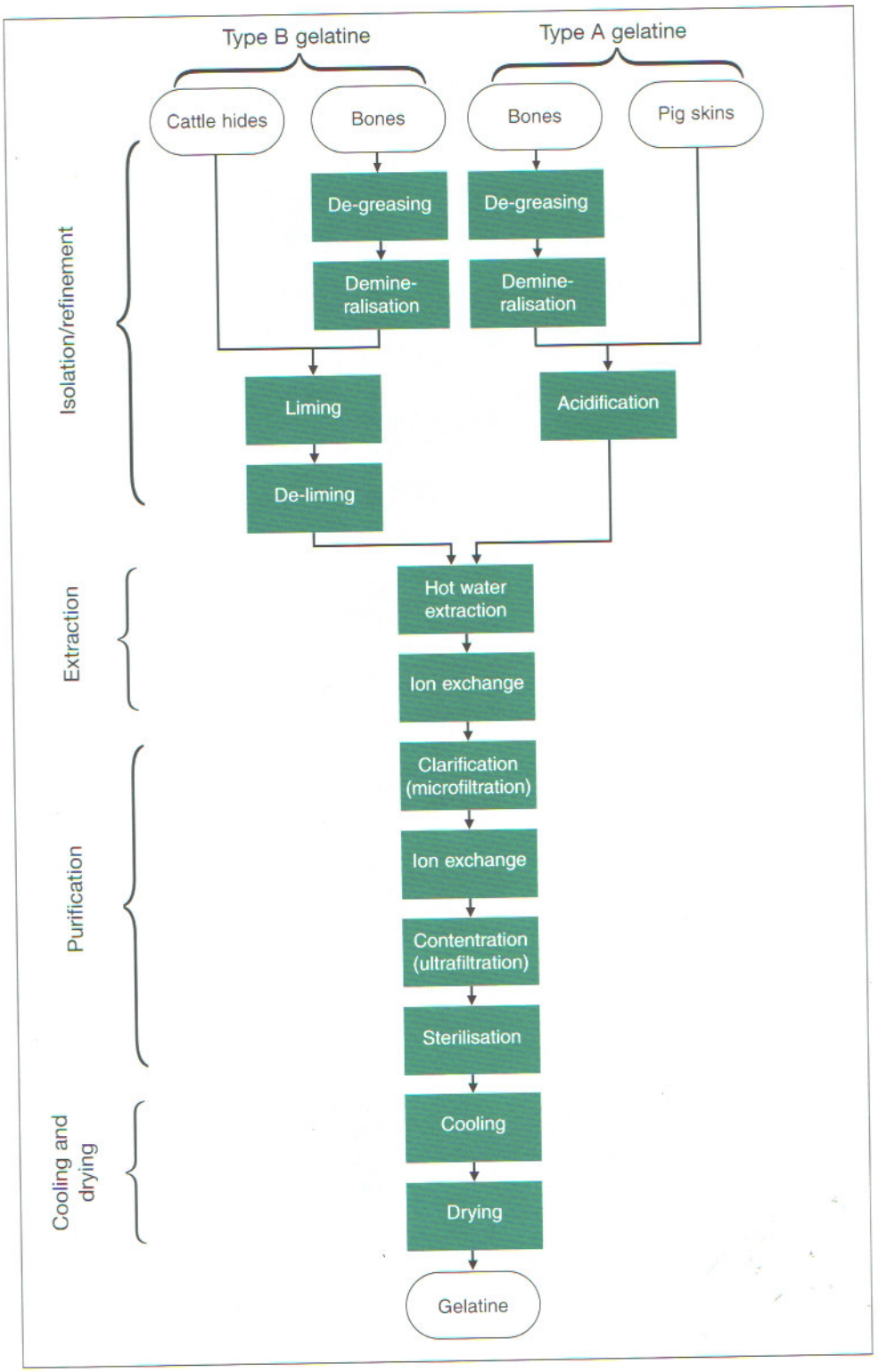
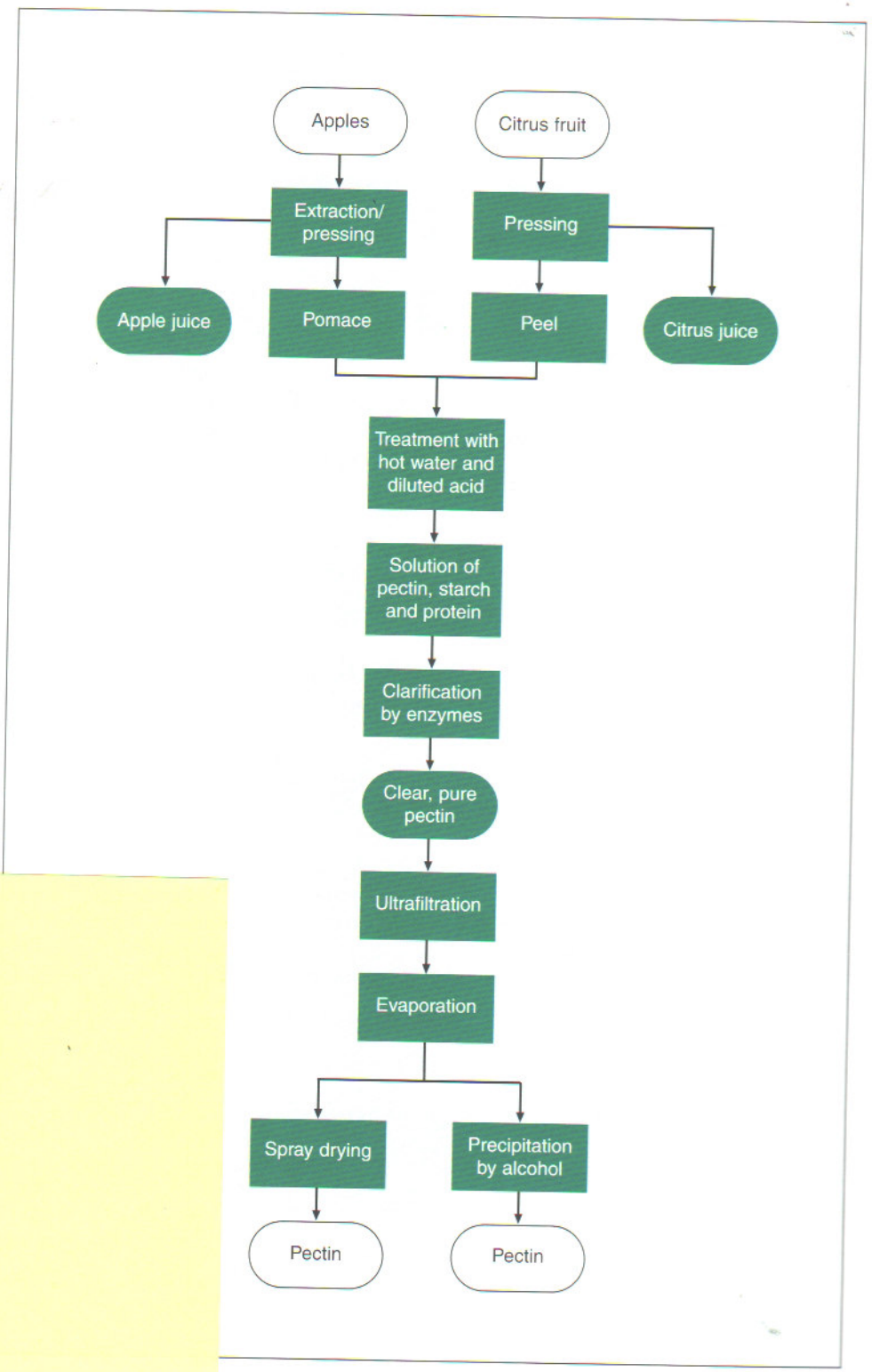


Figure 110: Gelatine manufacture. The gentle treatment using membrane concentration and purification improves the product quality.

Figure 111: Several molecular separation processes such as MF, ion exchange and UF are used in the manufacture of pectin.



Compared with animal protein, vegetable protein is a much more efficient way to produce protein. The FAO has estimated that one hectare of soy beans will provide enough protein to sustain a moderately active man for 5,560 days. In comparison, the same land based on cattle production, would only provide 192 days' supply of protein.

Soy bean products. The soy bean has served as the protein backbone of the East Asian diet for more than 2,000 years, and today it is an integral part of the diet of more than one billion people. The USA, Brazil and China are the leading producers.

The desirable components of soy beans are protein and fat, but there are also some undesirable components, which must be removed or reduced to increase the usefulness and functionality of soy bean products. Soy beans are known for the bitter taste and smell which develop during processing. This is caused by the formation of ketones and aldehydes produced by the enzyme lipoxidase, acting as a catalyst in the oxidation of the polyunsaturated fats. Furthermore, some of the oligosaccharides cause flatulence, while trypsin-inhibiting enzymes reduce digestibility.

Modern soy bean processing overcomes these problems and produces excellent soy based products. Figure 112 shows a general flow sheet of the main processing steps, provides an overview of the large variety of products which can be produced.

In many ways, the processing technologies are similar to those of milk, and many of the products resemble dairy-based products. UF is used for concentrating the proteins, following the production of the soy milk base.

The use of UF for manufacturing soy products usually results in higher yields because of the inclusion of whey proteins which are normally lost with conventional manufacturing methods. The whey proteins may also contribute to superior functional properties of the UF soy products.

Both spiral-wound, tubular and plate-and-frame systems can be used for processing soy products.

Recovery of CIP chemicals

Recovering caustic soda and acid used in CIP systems is becoming increasingly important, both from an environmental and an economic viewpoint.

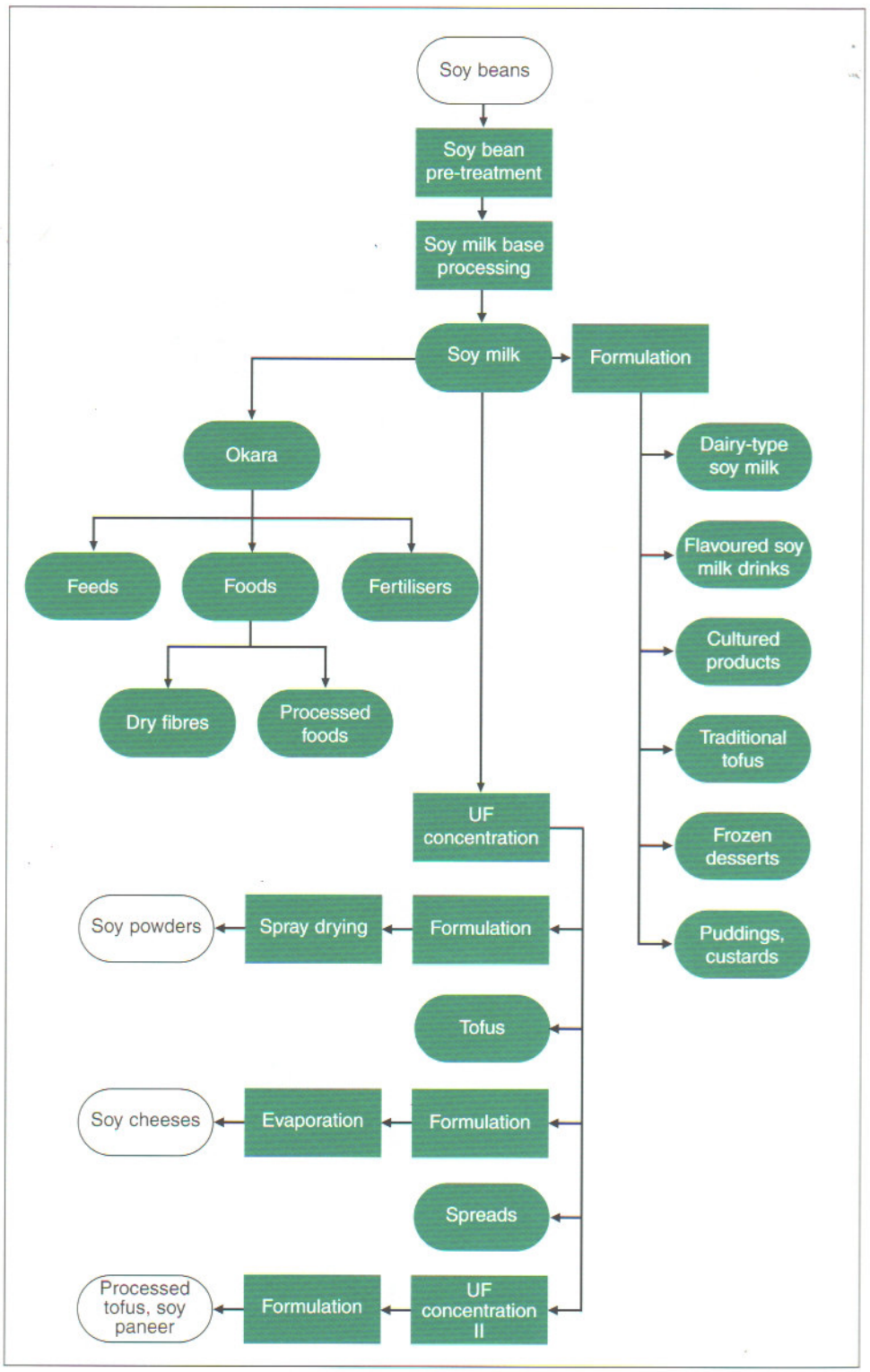
CIP involves alkaline detergents, typically caustic soda (NaOH) and nitric acid (HNO_3). However, heating surfaces are often cleaned with both alkaline and acid detergents. Normally, detergents are reused a number of times and when too degraded and polluted for further use, dumped into a sewage system. In the cleaning of evaporators and dryers, the cleaning solutions are often polluted to a degree where reuse would be futile.

Detergents account for a considerable part of total cleaning costs and clean water and waste disposal costs are increasing rapidly. Therefore, a profitable method for recovery of the detergents is becoming increasingly attractive.

Membranes have been used for CIP chemical recovery for the past 15-20 years. Normally, the systems have been based on ceramic UF or MF membranes. Only recently, has a system based on an organic NF membrane been developed. The NF membrane is resistant to both strong caustic and acid solutions, and can operate in the full pH range (pH 0-14). The CIP solution is separated into two streams:

- A permeate, which is clear and contains the purified caustic or acid

Figure 112: Soy milk products are the backbone of the East Asian diet, and membrane filtration is increasing the quality and variety of soy milk products.



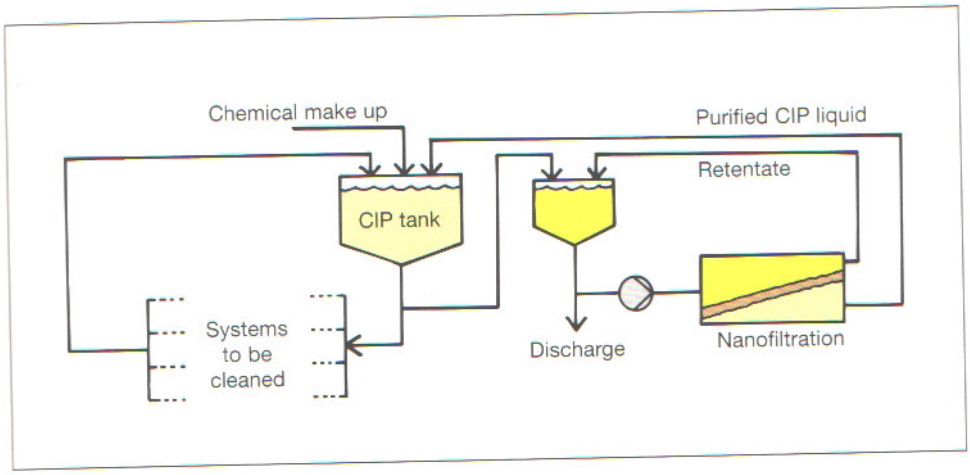


Figure 113: Recovery system for CIP chemicals. By using a specially designed NF system, it is possible to increase the reuse of chemicals far beyond what has been known so far.

- A concentrate, which contains all the soluble material and the main part of the organic material removed in the CIP process

The membrane is based on a tubular configuration and can handle solutions that contain fines, sediments and small particles. Typical CIP solutions from which chemicals are recovered using this system are:

- CIP systems in dairies and other food industries
- Dairy and food processing equipment in general
- Bottle washers in breweries
- Evaporators and dryers

Figure 113 shows a CIP system including a chemical recovery unit. The NF membrane has a molecular cut-off value of 250-300. This gives a COD rejection of more than 90% which is much higher than the rejection obtained with UF or MF membranes. The process enables 95% reclamation of caustics and acids, and 95% reclamation of water. This reduces chemical, waste disposal and water costs considerably. The concentrated waste material can be diafiltered in order to remove minerals, thus making it possible to use the remaining liquid for animal feed.

Biotechnology

The term biotechnology covers a wide range of biological processes used for the production of a variety of products from foods, flavours, organic chemicals, enzymes and pharmaceutical products to fuels and products for the agricultural sector.

Bio-catalysts are usually involved, such as enzymes, micro-organisms, plant cells or animal cells. Sometimes the bio-catalysts themselves are the end products. Biotechnology most frequently refers to the genetic manipulation of micro-organisms such as yeasts, bacteria and fungi.

Membrane filtration is used in many areas for the separation of cells from a fermentation broth and for the recovery of valuable fermentation products, such as proteins, enzymes, and antibiotics. In other instances, membranes are used in bio-reactors where they serve as supports for enzymes and micro-organisms and also allow the reaction and separation of the product to occur in a single stage.

Production of pyrogen-free water, as illustrated in Figure 114, is an important application for membranes in biotechnol-

ogy processing. This was described in more detail in the section on ultrapure water at the beginning of this chapter.

Figures 115-121 give a general overview of the various aspects of biotechnology. The processing is commonly divided into the following key areas:

- *Up-stream*
  - media preparation (Figure 115)
  - reduction of microbe content (Figure 116)
- *Process*
  - cell recycling (Figure 117)
- *Down-stream*
  - cell debris removal (Figure 118)
  - cell harvesting/cell washing (Figure 119)
  - concentration/purification (Figure 120)
  - concentration (Figure 121)

In all these areas, membrane filtration has a role to play, but especially in down-stream processing where membranes have proven to be an excellent tool for improvements in the manufacture of biotechnology products.

Enzymes

Enzymes are proteins which can catalyse chemical processes without being altered themselves. Even though enzymes have been used for thousands of years, it is only during the past decades that large-scale production has made enzymes more commonplace. Enzymes are used not only in cheesemaking, beer and wine production and in detergents, but they are also a natural part of the metabolism of living beings.

Enzymes are produced by extraction of plant and animal tissues as well as by microbes. In all instances, the solutions containing the enzymes are rich in low molecular weight compounds, such as salts and metabolic products. Removal of these compounds can be effected by different separation technologies, but UF and MF are most effective, due to the fact that they are 'non-destructive' technologies, able to combine molecular separation, purification and concentration of the biochemicals.

Membrane filtration is a common unit operation in most enzyme manufacturing today. Even though flux rates are sometimes low and membrane lifetimes short, the advantages compared with traditional processing are usually so large that the financial benefits clearly justify their use. Table 33 gives a selected overview of the range of enzymes being isolated by membrane filtration. The enzyme solu-

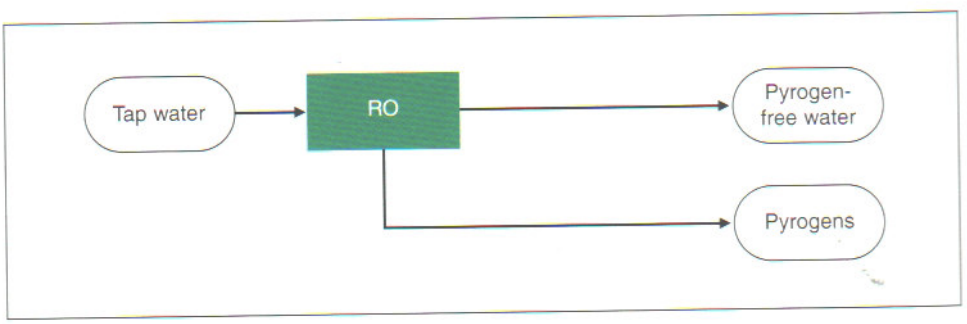


Figure 114: Pyrogen-free water.

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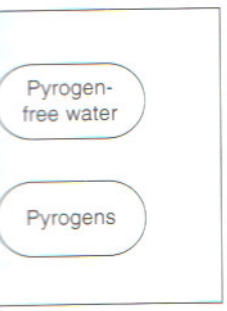


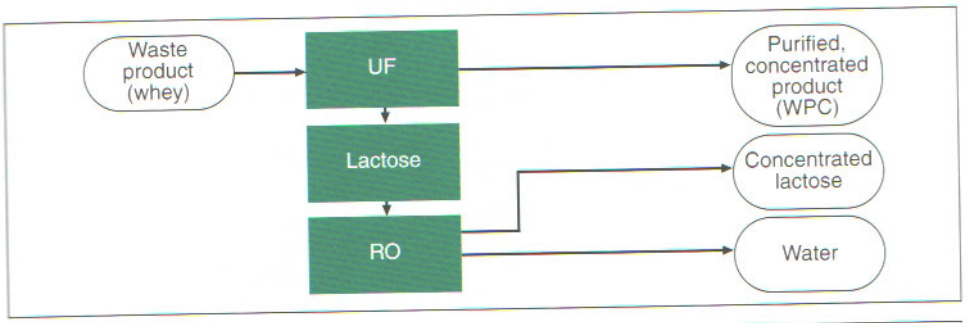


Figure 115: Media preparation.

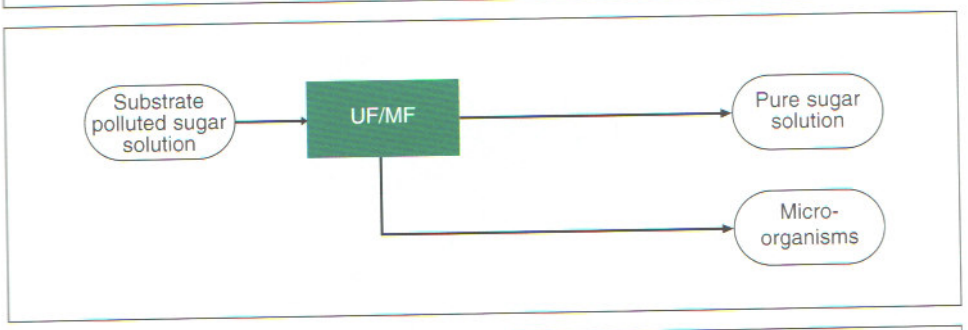


Figure 116: Reduction of microbe content.

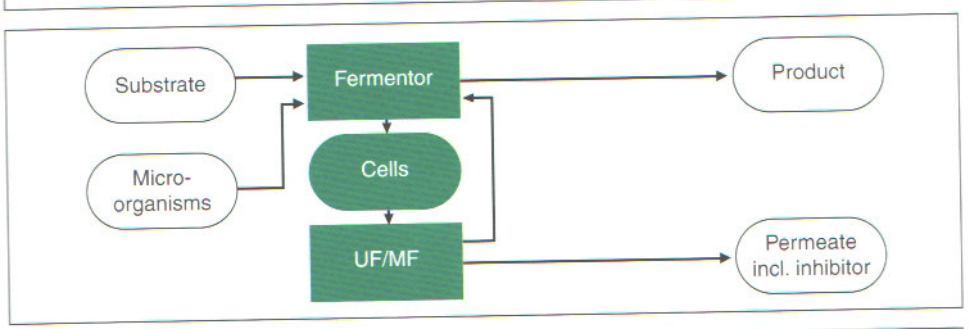


Figure 117: Cell recycling.

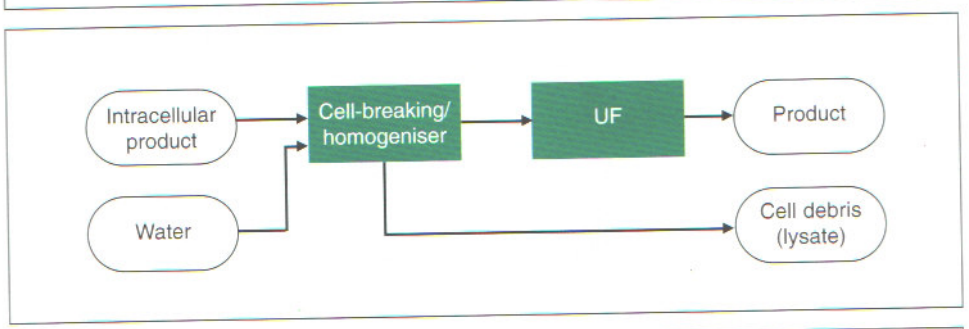


Figure 118: Cell debris removal.

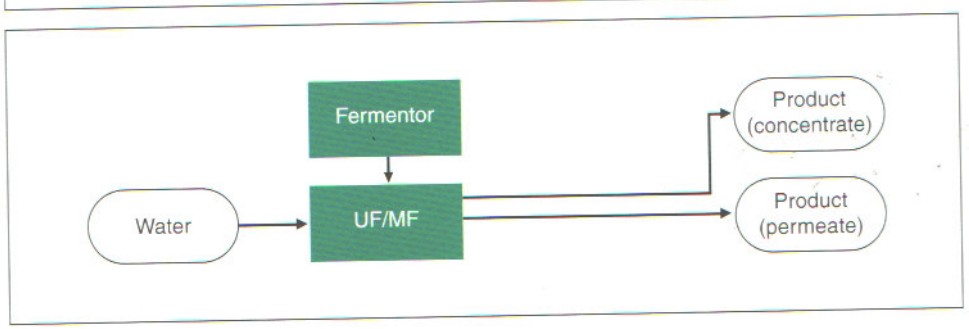


Figure 119: Cell harvesting and cell washing.

Figure 120: Product concentration and purification.

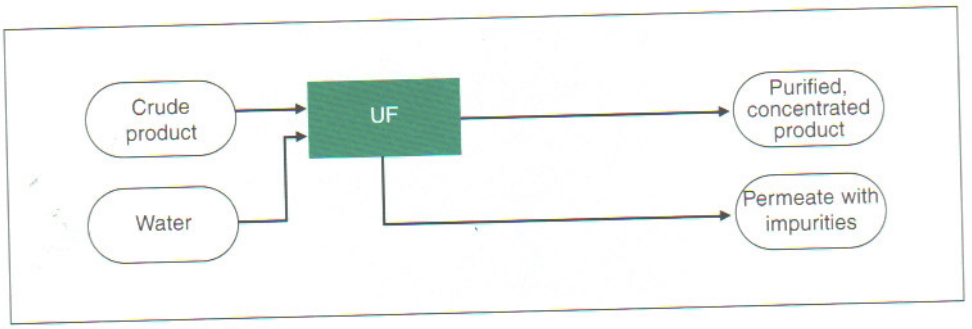
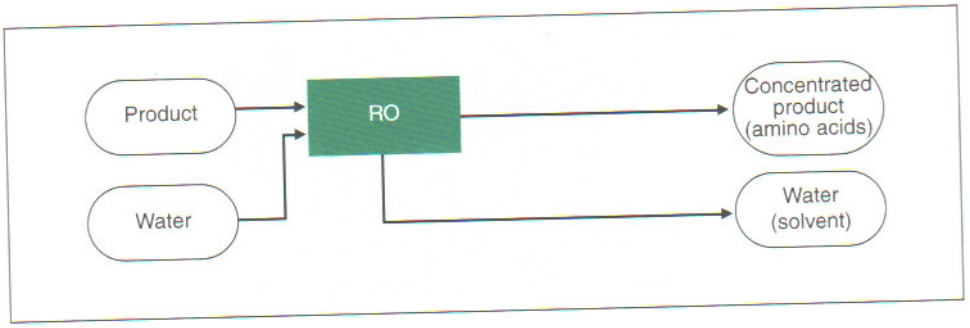


Figure 121: Product concentration.



tions sometimes have a high viscosity and the operations are carried out either batch-wise or in continuous systems. The temperature is usually kept low in order to maintain enzyme activity.

The membrane configuration varies depending on the type of enzyme, but the plate-and-frame system is often preferred, due to its ability to handle viscous products.

Antibiotics

Antibiotics are substances produced by micro-organisms which are capable of inhibiting the growth of – or even destroying – other micro-organisms. Many antibiotics are already on the market, and there are undoubtedly more to come. Today, penicillin accounts for approximately 25% of all antibiotic sales and tetracycline for 12-14%. Although the greater part of antibiotic production is for human treatment, antibiotics are used increasingly to control plant pathogens and food-spoilage organisms.

Figure 122 shows a general flow sheet for the production of antibiotics, indicating where membrane filtration can be used.

In the separation of cells from the antibiotics, UF or MF can substitute traditional processes such as drum filters and centrifuges, and a higher product yield can be obtained. If the antibiotic is intra-cellular, a cell disruption process is used, usually by means of a high-pressure homogeniser, and UF is used for separation of the product from the cell debris.

Concentration by RO and NF is less expensive than concentration by an evaporator. Since the removal of water takes place at a low temperature, the yield is higher due to less heat damage. Using NF makes it possible to remove low molecular compounds during concentration and this results in a more pure, higher quality product.

Table 34 shows a list of the various antibiotics produced by means of membrane filtration. Most types of membrane

Purified, concentrated product

Permeate with impurities

Concentrated product (amino acids)

Water (solvent)

eneral flow sheet
antibiotics, indicat-
filtration can be

lls from the antibi-
ubstitute traditional
n filters and cen-
product yield can
biotic is intra-cel-
process is used,
high-pressure
is used for separa-
m the cell debris.

nd NF is less
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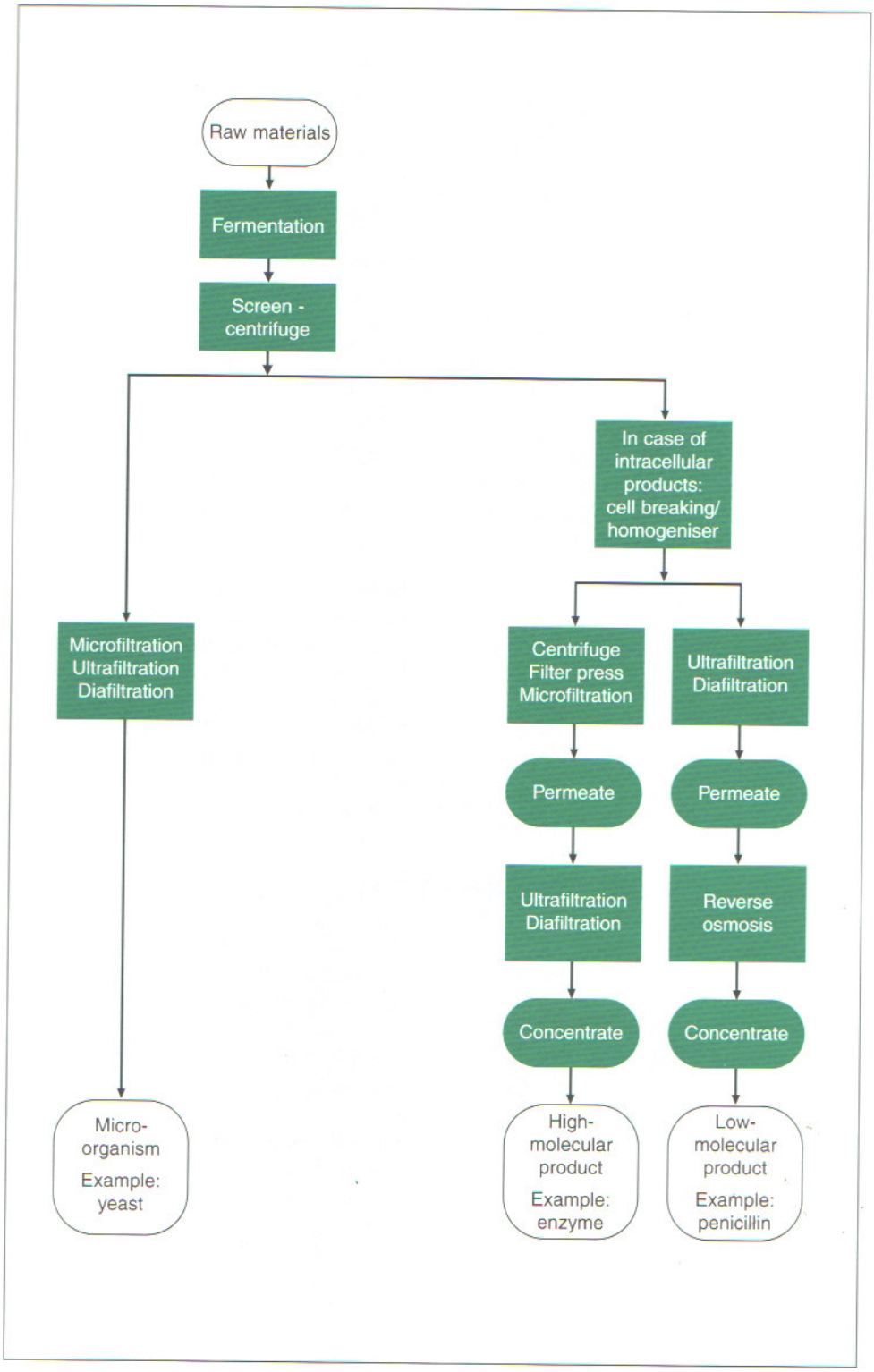


Figure 122: Manufacture of products in the pharmaceutical industry. Membrane filtration is used in yeast, enzyme and penicillin production.

Table 33: List of enzymes where membrane filtration is used in the production.

Microbial fermentation-based enzymes	Glucose isomerase
	Glucose oxidase
	Microbial rennet
	Pectinase
	Cellulase
	Protease
	Lactase
	Amylase
	Amyloglucosidase
Animal enzymes	Rennin/chymosin
	Chymotrypsin
	Lysozyme
	Rennet
	Trypsin
	Lipase
Plant enzymes	Bromalain
	Papain

Table 34: List of antibiotics which can be produced by membrane filtration.

Cephalosporin
6-Amino penicillanic acid
Clavulanic acid
Streptomycin
Neomycin
Polymyxin
Tetracyclin
Bacitracin
Tylosin

filtration systems can be applied to the manufacture of antibiotics, depending on viscosity, particle content, etc.

Membrane bio-reactors

Chemical and biological conversions using enzymes and/or micro-organisms as catalysts are commonly used in the production of organic chemicals, food products, pharmaceuticals, hormones, vitamins and other biological products.

Most of these processes are conducted in traditional batch type reactors, where the enzymes or microbial cells are used in their free or soluble form. This mode of operation has a number of disadvantages such as:

- Lower efficiency due to start up and shut down of each batch
- Product variations from batch to batch
- High capital costs for equipment due to low productivity
- Low utilisation of enzymes since each batch requires a new charge of enzymes
- Increased processing time due to substrate depletion and product inhibition

A way to overcome some of these problems is to immobilise the enzymes or microbial cells. This requires the chemical or physical attachment of the bio-catalysts to solid surfaces, or otherwise confining or localising them in a confined region or space with retention of their catalytic properties.

However, even though immobilisation has had some success, a number of problems and disadvantages have occurred. Loss in activity of the bio-catalyst, steric hindrance and high pressure drops in columns are just some of the challenges this technology has encountered. The use of synthetic semi-permeable membranes is seen as an alternative which might solve some of these problems.

The basic principle of the membrane bio-reactor is shown in Figure 123. A reaction vessel, operated as a stirred tank reactor, is coupled in a semi-closed loop configuration via a suitable pump to a membrane module containing the appropriate semi-permeable membrane. In operation, the reaction vessel is first filled with the substrate solution or slurry and the bio-catalyst is added at the appropriate concentration. The content of the reaction vessel is continuously pumped through the membrane module and recycled back to the reaction vessel. The membrane should be chosen to retain the bio-catalyst while minimising the retention of the product molecules. Since most enzymes have molecular weights in the order of 10,000-100,000,

UF membranes with an appropriate molecular weight cut-off can be used. When processing microbial cells, MF membranes with larger pores may be used.

When the reactor is in a steady state, product molecules small enough to permeate through the pores of the membrane are removed from the cycle while the bio-catalyst is recycled to the reaction vessel.

The total volume of the system is kept constant by matching the incoming flow rate to the volume of product leaving the system.

Hydrolyses of proteins and carbohydrates have successfully been carried out using this principle and it is expected that this concept will find further applications in the future. In many cases, the hollow fibre system has been applied as part of a bio-reactor system, due to its back flush capability.

Industrial applications

There are many industrial applications of membrane filtration processes and the scope of this book does not allow a complete review. In the following section some of the most common applications will be described.

Electrophoretic paint recovery

This was the first really large industrial application of membrane filtration. The electro-deposition of paint was introduced in the mid-1960s. The pieces to be painted are immersed in an aqueous solution of paint, and a voltage is made to flow between the piece to be coated and the paint tank or a fixed electrode.

After the electro-deposition of the paint was complete, the pieces were lifted out of the tank and the non-deposited, loose-

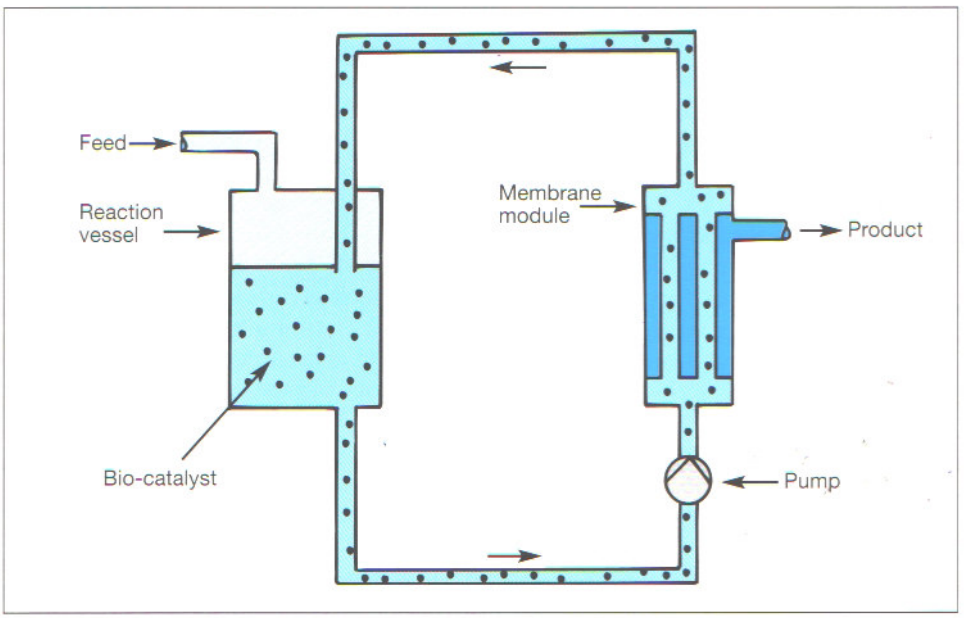


Figure 123: The bio-reactor. The membrane recycle reactor has substantial processing advantages in enzymatic processes, enabling continuous reuse of the enzyme in hydrolyses of for instance proteins and carbohydrates.

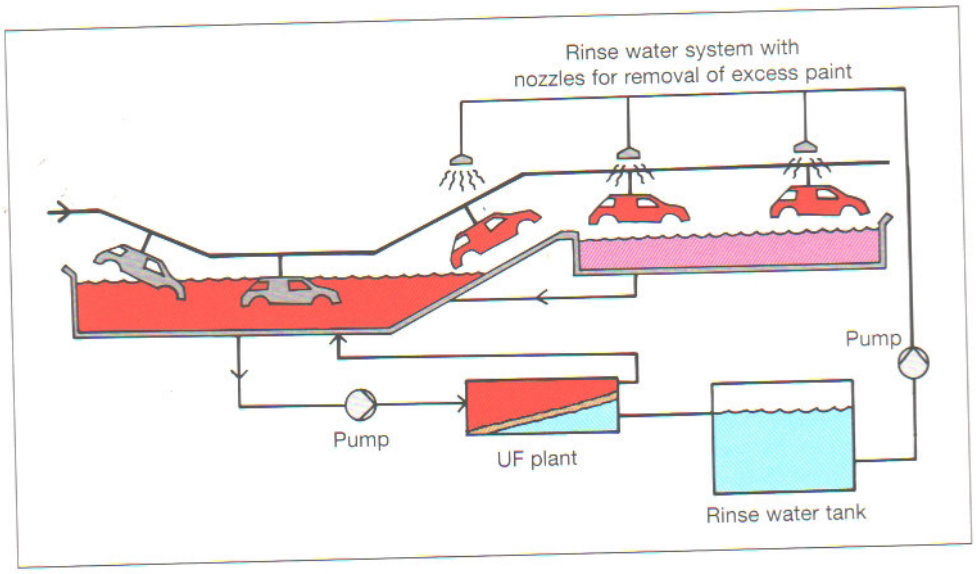


Figure 124: Using UF for recovery of electro-phoretic paint. The recovery system is widely used in the automobile industry, and is one of the most successful applications of UF.

ly adhering paint was washed off by a cascade of spray water jets, and the parts were then cured in an oven. The process is favoured universally because of its excellent, consistent, and defect free coating results, even on objects with sharp edges and recessed areas.

The water used for spraying off excess paint becomes contaminated and represents an environmental problem. UF is an ideal process solution for this problem.

Figure 124 illustrates how the UF system is coupled to the e-coat paint tank. The permeate, which is free of paint particles, is used in a closed loop, multi-stage counter-current rinse system. The system significantly reduces the operating costs of an electro-deposition system by reducing the consumption of de-ionised water and lowering the paint costs.

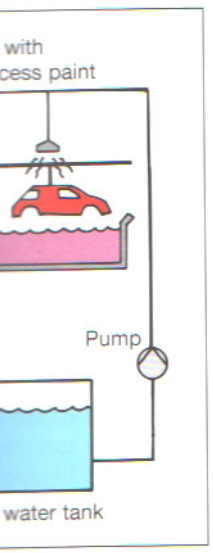
Successful operation of UF systems for paint recovery requires careful selection of the membrane type, system type and operating parameters. A high fluid velocity is required to minimise the concentration polarisation and fouling effects. Since the paint particles are charged negatively for cathodic paint systems, the membrane should be of a hydrophilic type with negatively charged groups, in order to prevent adherence of paint particles to the membrane surface.

The most commonly used systems are the hollow fibre and the tubular ½-inch systems. Originally, the leaf system developed by Dorr Oliver was also used extensively for this application.
Today, the paint recovery systems are used in car manufacturing plants the world over and several hundred systems are in operation. It is believed that electro-deposition of paint would not be economically viable without the use of UF paint recovery systems.

Oily waste water

A wide variety of industries generate billions of litres of oily waste water daily. Table 35 gives a survey of some of these industries and the origin of the waste water. In general, oily waste water may be grouped into the following three categories:

- Free floating oil
- Unstable oil/water emulsions
- Highly stable oil/water emulsions



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Free floating oil can be removed readily by mechanical separation devices which use gravity as the driving force. Unstable oil/water emulsions can be mechanically or chemically broken, and then gravity separated. However, stable emulsions, and particularly water soluble oily wastes, require more sophisticated treatment to meet today's effluent standards.

Using UF for treatment of oily waste water, means that the permeate becomes an oil free water phase which can usually be discharged to the sewer without any further treatment. The concentrate, which constitutes only a few percent in volume of the original solution, is an oil phase which can usually be incinerated or transported to a waste disposal plant. The membranes have to be selected carefully, depending on the industry and type of waste water.

Waste oil/water emulsions from cutting and grinding operations generally have a pH of about 10 and may contain various fouling components which will require both acidic and alkaline cleaning agents to recover the flux rates of the UF system.

Waste oil from steel rolling mills require membranes that are able to operate at 70°C on a continuous basis and can withstand alkaline cleaning agents.

Waste cutting oils typically contain 0.1-10% oil and grease. Concentrates containing 40-70% oil and solids are obtainable using UF. The membranes used normally have a cut-off value of 20,000-50,000 which gives a permeate with less than 10-100 ppm oil. The systems used are normal hollow fibres, tubular, and spiral-wound systems.

The textile industry

The textile industry is a large user of water and toxic and/or valuable chemicals such as dyes. Consequently, pollution control and water reuse are major concerns of this industry. It is beyond the scope of this book to give a more thorough description of the potential applications of membranes for pollution control, but the following example illustrates the potential.

The textile industry uses synthetic sizing agents such as polyvinyl alcohol (PVA)

Industry	Source of oil wastes
General metal working	Water soluble coolants, cutting and grinding oils, and lubricants used in machining operations
	Discharges from parts washer tanks, rinse waters and floor washings
Primary metal	Rolling and drawing oils used as lubricants and coolants in ferrous and non-ferrous operations
Waste collection	Emulsified and water soluble oil wastes collected by waste hauliers from various industries
Food processing	Natural fats and oils from animal and plant processing, particularly vegetable oil wastes
Transportation	Discharges from road tanker cleaning, discharges from oil tankers
Textiles	Natural oils from wool scouring, fabric finishing oils

Table 35: Industries where UF is used for the purification of oily waste water.

and carboxymethyl cellulose (CMC) in cotton blends. These sizing agents are expensive and non biodegradable, and consequently they pose a waste treatment and/or recovery problem. Both PVA and CMC can be recovered using UF.

Spiral-wound systems are most commonly used. Flux rates are quite low (10-15 lmh) and this requires large membrane areas. Typically, the plants contain up to 5,000 m^2 membrane area. The feed solution contains 0.5-1.0% total solids and the concentrate usually contains 14-16% total solids. The operating temperature may be as high as 70-85°C.

Dyeing of cotton is probably the largest dyeing operation in the world, and close to 50% of all dyeing is made with reactive dyes on cotton. Several studies have been made in order to find ways to reclaim water and chemicals in the dyeing process and it has been proven that large savings in time, water, energy and chemicals are possible, provided certain changes in dyeing and rinsing methods are accepted.

The electroplating industry

In the electroplating industry, the major pollution problems arise from the toxicity of the chemicals involved and the large volume of water used in the rinsing operations. The discharge of such rinse water into natural water streams or municipal sewer systems results in severe environmental pollution and reduction in the efficiency of biological water treatment processes. This is in addition to the loss of valuable chemicals and water. Such pollution problems and their consequences can be avoided by RO. Both the rinse water and the plating chemicals can be recovered and advantageously reused.

Figure 125 illustrates a two-stage RO plant in the nickel plating industry. The rinse water from the first rinse is fed to the first stage RO plant which has an 80% recovery rate of reusable water. This water is used for the second rinse and contains approximately 60 mg/l of nickel salts. The concentrate from the first stage RO plant is taken to the second stage RO plant. This has a 90% water recovery rate. The permeate is mixed with the feed of the first stage RO plant, while the concentrate, which contains 100,000 mg/l (10%) nickel salts, can be fed back directly to the plating bath. The rejection of nickel salts is 99% using CA membranes. Such a system may have near 100% nickel recovery, and 98% recovery of water. In many situations, the second stage RO system is replaced with an evaporator. The pH of the nickel plating solution is usually around 4-6, which is the ideal pH range for CA membranes.

When treating rinse water from chrome plating systems, the pH needs to be adjusted to 2.5 as a minimum for safe operation of CA membranes. The concentrate from the RO plant passes through a cation exchange column to remove sodium, calcium and iron. The cation purged concentrate then returns to the chrome bath as H_2CrO_4, identical to the composition in the chrome rinse bath. The retention of chromium salts is only 93%, which leaves too large amounts of plating chemicals in the permeate. Therefore, the permeate is passed on to a collection sump for conventional treatment and processing.

Altogether, RO is playing a significant role in water treatment in the electroplating industry and today it is possible to build zero-discharge waste treatment systems using combinations of different separation technologies.

The pulp and paper industry

The most important raw material in cellulose manufacturing is wood. The spent liquor from pulp production contains about 50% of the organic material present in wood. This consists of a complex

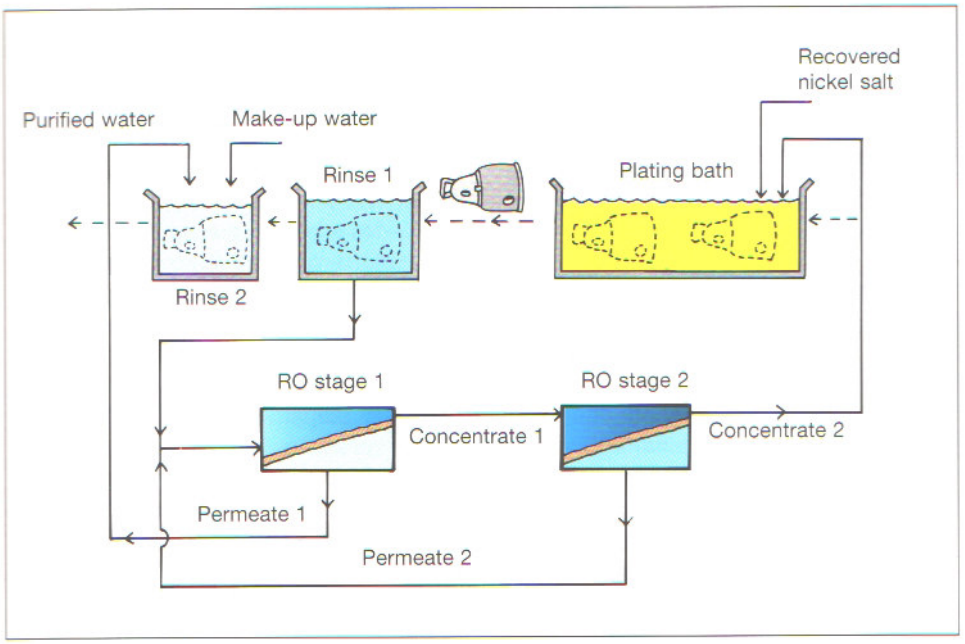

Figure 125: Reclamation of nickel in the plating industry. The nickel salts are concentrated up to 10% and returned to the plating bath. This is an application where CA membranes have proven to be very durable due to the low pH level.

mixture of organic break-down products and inorganic constituents from the cooking chemicals. The main constituent in the dissolved material is the binding material inherent in the wood - the lignin.

Lignin is present in the waste liquor in various modifications, depending on the process. The sulphite process converts lignin to lignosulphonates, the alkaline process produces alkali-lignin, whereas chlorinated lignin is the result of the bleaching process. Most of these components have high molecular weights, and this makes membrane filtration an interesting alternative process for fractionation and purification of lignin products from waste liquors.

'Black liquor' is the waste product from the so-called Kraft process for production of cellulose pulp. It contains 17-22% total solids of which 41% is alkali-lignin. In the manufacturing of glue for plywood and particle board production, the traditional phenol-formaldehyde resin is replaced by purified alkali-lignin. UF is the key to producing such purified alkali-lignin from black liquor as the raw material for the glue.

Sulphite waste liquor is the waste product from the sulphite process for production of cellulose pulp. It contains 12-16% total solids of which 52% is lignosulphonate. Table 36 shows the composition of sulphite liquor. The carbohydrate content is utilised commercially in the production of alcohol by fermentation of mannose and glucose in the crude liquor.

The lignosulphonates are concentrated and purified by UF up to a purity of approximately 80%. If diafiltration is applied, a purity as high as 95% can be obtained. Purified lignosulphonates are utilised as binders, dispersing agents, concrete additives and feedstock for chemical processing of, e.g. vanillin.

Probably the most important of all applications in the pulp and paper industry is the treatment of effluent from the bleaching of the Kraft pulp. UF is able to remove as much as 87% of the colour and 80% of the COD from the bleaching liquor.

Table 36: Composition of spent sulphite liquor.

Total solids (TS) 12-16%	% of TS
Lignosulphonates	52
Extractives	3
Poly- and oligosaccharides	6
Monosaccharides	23
Various organic compounds	11
Calcium	5

Pre-treatment is essential for trouble-free operation of the membrane filtration systems. A normal pre-treatment in this industry consists of sand filtration for fibre removal. Both plate-and-frame systems and tubular systems are used for processing the liquors.

The kaolin industry

Kaolin (china clay), is a fine white mineral powder used by the paper, porcelain, ceramics, paint and rubber industries among many others. Kaolin is the result of various geological processes converting feldspar over hundreds of millions of years. Chemically, kaolin is a hydrated aluminium silicate, and can be represented as follows:

$Al_2O_3 2SiO_2 2H_2O$

An important feature of kaolin is its extreme fineness, and even the coarser grades are finer than most talcum powders. The Chinese have used kaolin for a thousand years to make white porcelain, but it was only in the mid-eighteenth century that the value of kaolin was discovered in Europe.

Kaolin is produced in many countries with the USA, UK, and Ukraine among the largest producers. In a kaolin pit, kaolinised granite is broken up by water jets, resulting in a mixture of sand and clay in suspension, running to a low point in the pit where the clay and sand are separated by conventional classification processes. The clay fraction is pumped away for further refining and the sand is discarded.

In the refining processes, thickening tanks, hydrocyclones and centrifuges are used to remove remaining fine sand and mica. Magnetic separation, using powerful electro-magnets, removes titanium and iron oxide, which are harmful in the applications of kaolin. At the same time, the clay is sorted into grades of different quality, and other processes are used to improve properties such as whiteness and fineness.

The refined kaolin is piped to drying plants where it is first thickened in settling tanks, followed by further thickening in drum filters and filter presses. The filter cakes are cut up and fed into mechanical dryers, such as rotary dryers, fluid bed dryers or spray dryers.

UF is able to concentrate suspended kaolin from 20-30% solids to levels as high as 60%. The 60% suspension is still in a stable, liquid and pumpable form. Usually, the UF plant is placed at the pit, following the refining steps, and the concentrate is pumped through a pipeline to the drying station.

Spiral-wound elements can be used provided they are equipped with a wide spacer (48-100 mil). Furthermore, it has been possible to develop a spiral-wound element which can operate at 80°C giving a satisfactory flux as a function of the solids content.

The kaolin industry operates on a very large scale, and plant sizes can be in the order of 100,000 kg/h in feed rate, requiring more than 5,000 m^2 in total membrane area. The kaolin industry is interesting because it has demonstrated that membranes have applications in quite different, non-traditional areas. In this case, the technology has been taken successfully to the limits, in terms of sol-

id level, operating temperature, spiral-wound module design and total plant size.

The benefits are process simplification and reduction in processing costs. Furthermore, the yield, especially of the very small particle kaolin, is increased. This is because the membranes, unlike conventional filters, reject all kaolin particles.

The largest part of the kaolin produced is used in paper manufacturing, as a filler to give smooth texture and whiteness to the sheet. Also, in a fine particle clay form, together with adhesives for paper coating, it produces smoother, brighter and glossier surfaces, to allow for high quality colour printing. The second largest application is in the production of porcelain.

Electrodialysis

The industrial application of electrodialysis (ED) dates back to the 1950s when the process was installed in arid parts of the world like North Africa, Saudi Arabia, Iran and Iraq for desalination of brackish water to produce drinking water.

In the 1960s, a new generation of membranes with improved selectivity and reduced electrical resistance was developed in Japan. These membranes were used especially for the production of common salt from sea water. In recent years, ED has been used increasingly in the production of industrial process water as well as for treatment of certain types of waste water.

Water treatment

Desalination of brackish water is by far the largest application of electrodialysis, and it is estimated that more than 4,000 plants with a total membrane surface of 2.5 Mm^2 have been installed worldwide. A combination of ED and ion exchange makes it possible to reduce the production costs of water considerably, through savings in chemicals for regeneration of the ion exchanger. In many instances, the ED plant is also combined with other desalination processes like RO and NF, and sometimes UF or MF may be used for pre-treatment of the feed to the ED plant.

Electrodialysis reversal (EDR) is based on conventional ED where the polarity of the direct current driving force is periodically reversed. The reversal is typically performed at intervals of 15 to 20 minutes. During the reversal period, starting deposits and fouling formations are removed and discharged from the membranes. The process can be completely automated, and during the switch-over, the product water is temporarily discharged until the required salt level is re-established.

EDR was developed to solve operating and maintenance difficulties encountered when acids and chemicals were injected into the system to control scaling, and has become a rugged, self-cleaning membrane demineralisation process. Today, hundreds of EDR systems, the largest with capacities of 48,000 m^3 per day, are installed all over the world.

Concentration of sea water for production of common salt is used especially in Japan, Korea and Taiwan. The water is concentrated to a salt content of 20% and evaporated before being led to a system of crystallisers.

Whey treatment

ED has also found its way to the dairy industry, as mentioned in previous sections. For a number of years, several plants were installed to demineralise permeate from UF of whey, where demineralisation levels below 70% were required. However, ED plants suffer from some limitations, of which the following are the most important:

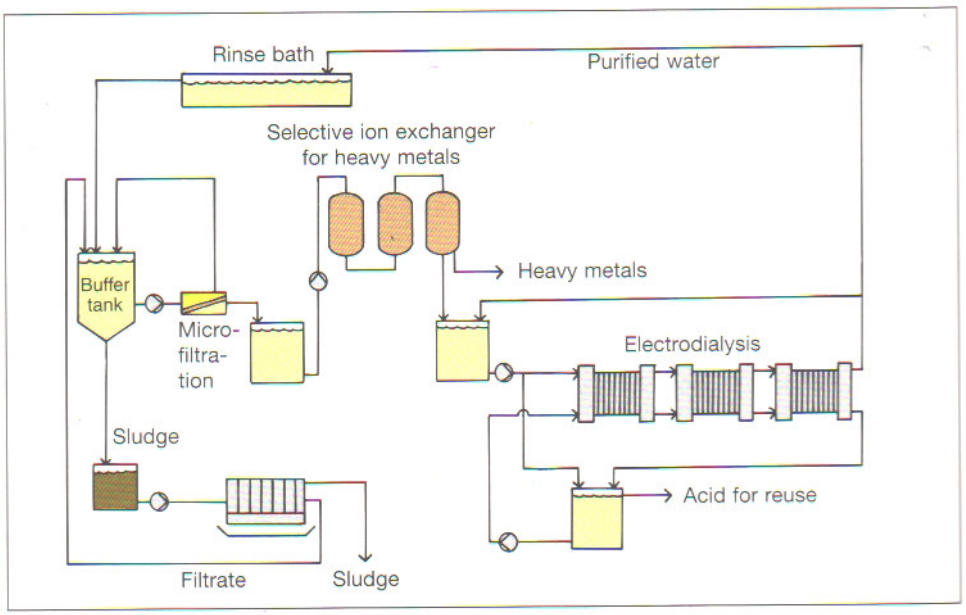

Figure 126: Recovery of chemicals in the production of accumulators. Recovery of acid and water using electrodialysis, ion exchange and MF is a good example of how the combination of molecular separation processes can solve complex environmental problems.

- Limitations in temperature (50°C) and alkaline pH (pH 9) make cleaning difficult, and normally the ED stacks have to be taken apart once every 2-4 weeks for manual cleaning
- Loss of lactose due to some leakage of lactose through the ED membranes
- Waste water from the plant contains lactose and phosphates, which may present a serious environmental problem.

The development of NF, where sodium chloride can be removed selectively during concentration of whey or permeate, has also presented an alternative way of partial demineralisation which for many applications may be more attractive.

It is estimated that more than 100 plants are installed in the dairy industry, corresponding to a membrane area of approximately 50,000 m^2.

Recovery of acid and rinse water

In the production of accumulators, the lead plates are treated with sulphuric acid followed by a water rinsing stage. The water used for rinsing contains lead and acid. Normally the rinse water is treated with milk of lime to form a precipitate of calcium sulphate (gypsum) and metal hydroxides.

In order to recover both acid and water, a system as shown in Figure 126 can be installed. The rinse water containing acid and heavy metals is pumped to a buffer tank. An MF plant is coupled to the buffer tank for removal of traces of sludge. The permeate goes through a selective ion exchanger which captures the heavy metal ions. The diluted acid solution goes from the ion exchanger to an ED plant, where the acid is concentrated to more than 10% and can be returned for treating the lead plates. The purified water from the ED plant is also returned for rinsing the lead plates. Finally, the sludge is removed from the conical bottom of the buffer tank, and de-watered in a filter press system.

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The system has made it possible to convert a heavily polluting industry into a more environmentally friendly industry, with recovery and reuse of both water and chemicals through an intelligent combination of molecular separation processes.

Gas separation

Gas separation is an emerging technology and the number of applications is gradually increasing.

Recovery of volatile organic compounds

The emission of waste air streams containing low or medium concentrations of organic solvents is an increasing environmental problem. Aside from this, these solvents constitute a considerable amount of lost energy and valuable resources. The total amount of solvent emission is huge. An estimate for the USA, the largest industrial nation in the world, is more than 22 million tonnes of solvent emitted annually.

Treatment of contaminated air streams, and subsequent solvent recovery, has been a constant issue during the past decades. In chemical engineering, many separation processes are applicable. These include condensation, absorption and adsorption, which enable solvent recovery, or incineration without solvent recovery.

A new promising technology, however, is membrane vapour separation using elastomeric polymer membranes. Figure 127 shows a flow diagram for a membrane vapour separation process.

The vapour/air mixture is first compressed to 2-15 bar. The compressed mixture goes through a condenser where it is cooled. A portion of the organic vapour condenses and is directed to a solvent storage tank for recycling. The non-condensed portion of the vapour/air mixture passes across the surface of a composite membrane which is much more permeable to organic vapours than to air. The membrane separates the gas into two streams: a permeate stream containing most of the remaining solvent vapour from the condenser and a solvent depleted stream essentially stripped of organic vapour. The permeate stream is drawn back into the inlet of the compressor, and the solvent-depleted air is vented from the system. In order to provide the driving force for permeation, a lower vapour pressure must be maintained on the permeate side of the membrane than on the feed side. This pressure differential can be obtained by compressing the feed upstream of the membrane modules and by using a vacuum on the permeate side.

The membrane elements for gas separation are made as spiral-wound elements, plate-and-frame or hollow fibre systems. The membranes are thin film composite types usually made from PS cast on a support fabric, where the PS layer is covered with a selective barrier of polydimethylsiloxane (PDMS).

The membrane vapour separation systems are used for recovery of organic air pollutants from a variety of processes, including reactors, storage and transfer operations for gasoline, dryers, refrigerators, and sterilisers.

Table 37 shows a list of typical air pollutants recoverable by membranes.

Drying of compressed air

Drying of air in compressed air systems is normally done by means of adsorption in a suitable medium, followed by a regenerative desorption step after the medium has saturated. The disadvantage of this process is that a double system is necessary to switch between one system in operation and one system being regenerated. A new technology based on mem-

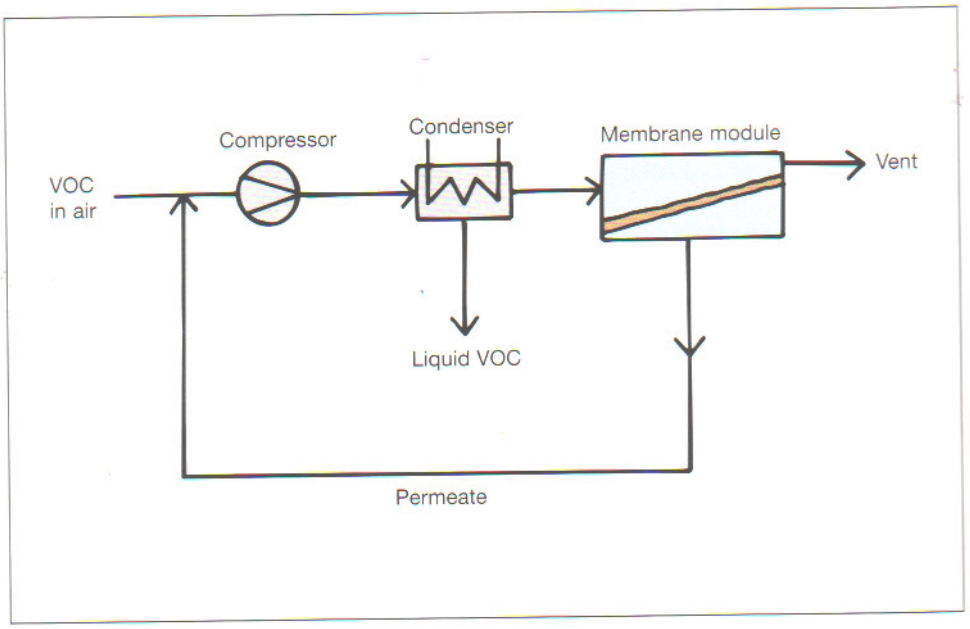


Figure 127: Recovery of volatile organic compounds (VOC) by means of gas separation. This process is used for recovery of air pollutants from reactors, storage and transfer operations for gasoline, dryers and refrigerators.

brane separation has been developed, using a membrane only permeable to water vapour.

The membrane is produced in a hollow fibre form, where the inside of the fibre is coated with an ultra-thin selective barrier. The active skin layer performs the actual separation of water vapour from air, allowing water to pass more than 10,000 times more easily than air.

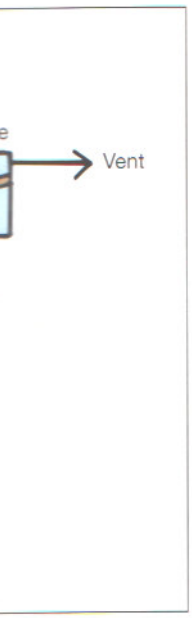
The wet compressed air is fed to the hollow fibre module, passing the membranes on the inside. The water vapour passes from the compressed air feed stream across the membrane into the module shell. The driving force is the fact that the concentration of water vapour in the compressed air feed is always greater than the water vapour concentration on the shell side of the membrane. This can be achieved by allowing a purge flow of dried air to literally sweep the water vapour away from the membrane surface on the shell side.

Table 37: Air pollutants which are recoverable by membrane-based vapour separation processes.

Acetaldehyde
Acetone
Acetonitrile
Benzene
CFC-11
CFC-12
CFC-113
Chlorine
Chloroform
Ethylene oxide
Hexane
Methanol
Methyl bromide
Methyl chloroform
Methyl isobutyl ketone
Methylene chloride
Propylene oxide
Styrene
Toluene

Pervaporation

The first industrial plant based on pervaporation (PV) technology was built in Brazil in 1982 for production of anhydrous ethanol, and since then more applications have emerged in the chemical industry.



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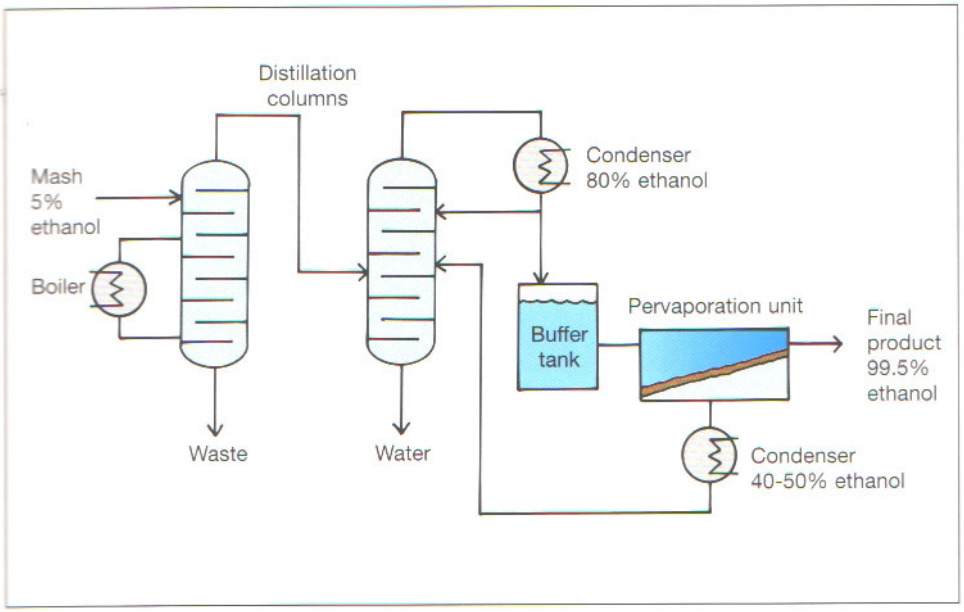


Figure 128: Integrated distillation and pervaporation recovering pure ethanol. Pervaporation is able to break azeotropic mixtures and reduce the energy consumption for recovery of pure organic solvents.

Figure 128 shows how PV can be coupled with distillation to produce pure ethanol from alcohol produced by fermentation. The fact that the last water is removed by a membrane process at a low temperature reduces the energy consumption for the total process by approximately 30%. In the case of a mixture of isopropanol in water, the corresponding reduction in energy consumption would be in the order of 62%.

Also in the food industry, new applications are emerging. The advantages of PV are primarily that low concentrations of components can be removed from solutions under very mild conditions without heat treatment.

Aroma recovery is a promising application for PV. Aroma compounds are typically organic compounds such as alcohols, aldehydes and esters, which are extremely volatile. An evaporative concentration process would therefore result in considerable losses, and in some cases even a total loss of aroma compounds in the evaporator. It is possible to recover some of the aroma by means of an essence recovery system based on partial condensation and scrubbing.

A more gentle way for aroma recovery could be to use PV to separate the aroma, either prior to the evaporator or from the evaporator condensate. These studies are still in their infancy, but it is believed that an enrichment factor of more than 500 can be obtained for the various aroma compounds in fruit juices.

15 Application of resin-based processes

Ion exchange is by far the largest industrial application of resin-based processes. Chromatography is mostly known as an analytical tool in laboratories for separation and identification of chemicals in complex mixtures of various components.

During the past decades, several processes such as RO and NF have been developed which are able to remove ions from water. Even though these processes may be seen as competitive to ion exchange, the situation is more likely that these processes are complementary to each other.

Ion exchange uses a lot of chemicals for regeneration, and this is becoming an increasing environmental problem. In many cases RO may relieve an ion exchange plant by removing the bulk of the ions.

The rapid development in biotechnology has increased the demand for more sophisticated separation processes to capture very small quantities of valuable substances in a mixture containing many other components.

Chromatography is increasingly used in the recovery and purification of various pharmaceutical products. Lately, chromatography has also been applied in the dairy and food industries for separation of complex mixtures of proteins, or for removal of specific components from food, beverage or dairy products.

Even though the potential of using chromatography on an industrial scale has been known for a long time, it is only through recent developments of improved resins and processing concepts such as radial flow chromatography that this potential can be commercially realised on a large scale.

Ion exchange

Ion exchange is used in a large number of industries in various applications for purification and recovery processes.

Water treatment

The use of ion exchange for treatment of water and a variety of effluent streams is by far the largest application. The recovery of pure water from spent process and effluent streams is becoming increasingly important.

Hard water causes problems both for industrial and domestic use, due to scaling and increased use of soap. Softening water by means of ion exchange is now commonplace. The water softener consists of a strong cation resin. When the water passes through the column, the calcium and magnesium ions in the water are replaced with sodium from the resin. The resin is then regenerated with a concentrated sodium chloride solution.

This process is widely used in various industries and for many domestic applications. Most automatic dishwashers contain an ion exchanger for softening the water in order that glasses and dishes look sparklingly clean after drying. The softening process does not decrease the total salt content in the water, since calcium and magnesium ions are merely exchanged for equivalent quantities of sodium ions. However, there is some increase in the mass of dissolved solids due to the molecular weight and charge

differences between the sodium ion and magnesium and calcium ions.

Water, free of all dissolved electrolytes, is said to be demineralised or deionised. Such water is essential for many industrial operations. This is especially true for water used in modern high-pressure boilers. Increasingly, the pharmaceutical industry, the food processing industry, the semiconductor industry and the nuclear industry also require the utmost purity of water.

This is achieved by ion exchange systems consisting of both a strong cation and a strong anion exchanger, followed by a mixed-bed ion exchanger. Under ideal conditions, such a system produces water with a conductivity as low as 0.04 µS/cm and 0.002 ppm silica, which is sufficient to fulfil the demands for water in high-pressure boilers.

Effluent treatment

Ion exchange is used for treating various effluents arising from metal finishing processes, such as plating and anodising. Thus, in chromium plating, the chromate ions (CrO_4^-) are removed with an anion exchange resin and converted to sodium chromate (Na_2CrO_4) by regeneration with sodium carbonate (Na_2CO_3). After passage through the acid form of a cation exchange column, the sodium chromate is converted to chromic acid, ready for reuse.

Ion exchange is also suitable for treating effluents from processes like paper manufacturing, photographic processing, leaching, zinc smelting and metal-pickling.

The most difficult waste disposal problems arise from the effluents produced during the processing of spent nuclear fuel. Increased restrictions on the discharge of liquid radioactive wastes have re-established the role of synthetic aluminosilicate exchangers, which are more stable towards high temperature and radioactive breakdown than the resins.

Carbohydrate

The principal applications for ion exchange are softening, decolourising and demineralising.

Softening is used in the beet sugar industry to reduce the calcium content of the purified sugar juice to avoid scale formation during evaporation. The same effect can be achieved by adding sodium carbonate (Na_2CO_3), but this requires addition of a surplus of sodium ions, which will lead to increased losses of sugar in the molasses. The ion exchanger used in sugar juice softening is a strong cation exchanger regenerated with a concentrated sodium chloride solution as in water softening.

The use of a strong base resin for decolourising sugar liquors is widely practised in the sugar industry. The pigments are organic anions which are absorbed by weakly cross-linked strong base gels and resins. Although the organic impurities tend to poison the resin, poor thermal stability is the main determining factor in the useful life of the resin in such operations.

Strong acid resins in the hydrogen form catalyse the inversion of sucrose to glucose and fructose. This property is used in the production of liquid sugar syrup from crystalline sugar.

Demineralisation of sugar juices is normally done by an anion exchanger in order to avoid the formation of an intermediate acid solution. This step is then followed by passage through a cation exchanger.

Whey treatment

Ion exchange is used for treatment of whey where high levels (90%) of demineralisation are required. The whey first enters a strong cation exchanger, loaded in the hydrogen ion form, and continues through a weak anion

exchanger in its hydroxyl ion form. Once a day, the columns are disinfected with a small amount of active chlorine solution.

Whey contains approximately 0.7% salt which is a high salt content for an ion exchanger. It leads to a high consumption of regeneration chemicals, which accounts for 60-70% of the total operating costs. Furthermore, some losses of whey protein will occur in the columns due to the substantial variations in pH during the ion exchange processes.

Using NF for part removal of sodium chloride is a good way to improve the economy in ion exchange processes.

The Swedish Dairies Association, SMR, has developed an alternative ion exchange process, where the whey is first passed through a weak ion exchanger in its hydrogen carbonate (HCO_3^-) form, followed by a weak cation exchanger in its ammonium (NH_4^+) form. The release of hydrogen carbonate and ammonium ions forms ammonium bicarbonate (NH_4HCO_3), which decomposes to ammonia (NH_3), carbon dioxide (CO_2), and water when heated during the subsequent evaporation of the whey. When the released ammonia and carbon dioxide are absorbed in water, ammonium bicarbonate is re-established and can be used for regeneration of the ion exchangers. This process operates with small variations in pH (6.6-8.2) resulting in minimum damage to the whey proteins. The process can also operate at a low temperature (5-6°C) thereby improving the bacteriological conditions during processing. The operating costs are reduced by 30-70% compared to conventional ion exchange processes.

Cation exchangers are also used for inversion of lactose in whey or permeate into galactose and glucose. This product can then be used as a sweetener.

Chromatography

While membrane filtration and ion exchange processes have experienced a rapid and successful growth in recent years, chromatography is still to a large extent viewed as a tool for identification and separation of chemical compounds in the laboratory, and for development and production in the biopharmaceutical industry.

However, the role for chromatography in the biotechnology industry is also tremendous. Without chromatography for the capture, purification and final polishing of biological macro-molecules, the world would be different today. The successful use of chromatography in this sector has made a valuable contribution to the speed of R&D, and consequently reduced time-to-market. It gives an overall improvement in the production economy of a wide range of pharmaceutical products.

In terms of volume, the production in the biotechnology area is quite small, compared to the volumes in the food, dairy and beverage industries. So far, the use of chromatography in these industries has been quite limited, because of the difficulties in scaling up to large volumes and because of the high price of both resins and columns.

There is an ongoing need in the food, dairy and beverage industries to bring new products onto the market and to reduce manufacturing costs. Separation technology is one of the means by which these industries can achieve such goals.

In the wide range of separation processes, chromatography is the only one that offers the unique advantage of selectively separating components from complex mixtures, based purely on their chemical and molecular properties.

During the past couple of decades, a new generation of chromatography resins and columns have been developed, and these new technologies are beginning to play a role, also in the dairy, food and beverage industries.

In the following section, the industrial applications of chromatography are reviewed. The applications of chromatography in laboratory science and in the biotechnology sector are very comprehensive and readers are referred to the specialist literature on this subject.

Whey protein separation

The separation of whey into WPC and permeate has already been described (cp. Figure 92). Direct UF of normal composition sweet whey increases the protein concentration to 65% protein on TS. Diafiltration can increase the protein content to approximately 85% protein on TS. The main disadvantage in using UF for protein concentration is the fact that the remaining fat content in the whey follows the protein into the final product.

The presence of fat and denatured proteins limits some of the applications of WPC in the food industry. This is particularly true for functional properties such as gel strength, blandness, whipping characteristics and emulsification capabilities.

In the mid-1980s, a system for producing WPI based on ion exchange chromatography was developed in the UK by Bio-Isolates and later licensed to Davisco in the USA. The system is based on a chromatography resin made from regenerated cellulose which has undergone hydroxypropylated cross-linking to give an improved physical stability of the final matrix.

Such resins are highly porous and hydrophilic. Even though they are physically robust, they will deform under pressure. They are quite chemically robust but will degrade in strong acid and oxidising agents. Also, their swelling properties alter on exposure to changes in pH and ionic strength. These properties make them difficult to use in a column system and make them better suited for a stirred tank system.

The active groups are strong acid ligands (SP/sulphopropyl) and strong base ligands (QAE/quaternary aminoethyl) which provide an ideal protein exchange mechanism.

In the stirred tank system, a batch of whey is slurried with a pre-determined volume of ion exchange resin until adsorption has occurred. Then the deproteinised whey is removed, the ion exchange resin is washed and the protein is desorbed into water using acid or alkali and/or mineral salt. The protein solution is concentrated by UF and finally spray dried.

The disadvantage of the process is the fact that not all proteins can be extracted, due to the equilibrium conditions in the stirred tank system. Table 38 shows a comparison between WPI and WPC. Even though the operating costs are increased considerably using this system, the higher price can be justified by the higher sales price that can be obtained for applications where whipping, water binding, emulsification and gelation properties are of high value.

Table 38: Comparison of the composition of WPI and WPC produced by the Bio-Isolate process.

		WPI Whey protein isolate	WPC Whey protein concentrate
Protein	%	92.0	75.0
Fat	%	1.0	6.0
Ash	%	2.0	3.0
Lactose	%	0.5	11.5
Moisture	%	4.5	4.5

New radial flow chromatography processes involving various combinations of column design, resin selection and process technology make it possible to process whey into the individual whey proteins like α-lactoglobulin, β-lactalbumin, bovine serum albumin, immunoglobulin and lactoferrin. It is also possible to produce WPI with a protein content higher than 90%, containing the total number of natural proteins in their original form.

Figure 129 shows a process diagram for production of WPI or IWP.

A 1,000 litres column is able to treat approximately 150,000 litres of whey per day. This is based on a cycle time for the column of 40-60 minutes, and a load per cycle of 7 column volumes. An industrial plant would consist of a number of parallel columns.

The release of the proteins from the chromatography resin is achieved by means of appropriate buffer solutions adjusted to a specific ionic strength. In this way, the release of the individual proteins can be controlled. The protein solutions are concentrated using UF, which allows reuse of the buffer solutions.

Figure 130 shows the composition of WPI and two types of IWP. The fat content is remarkably low (< 0.5%) as well as the lactose content (< 0.1%).

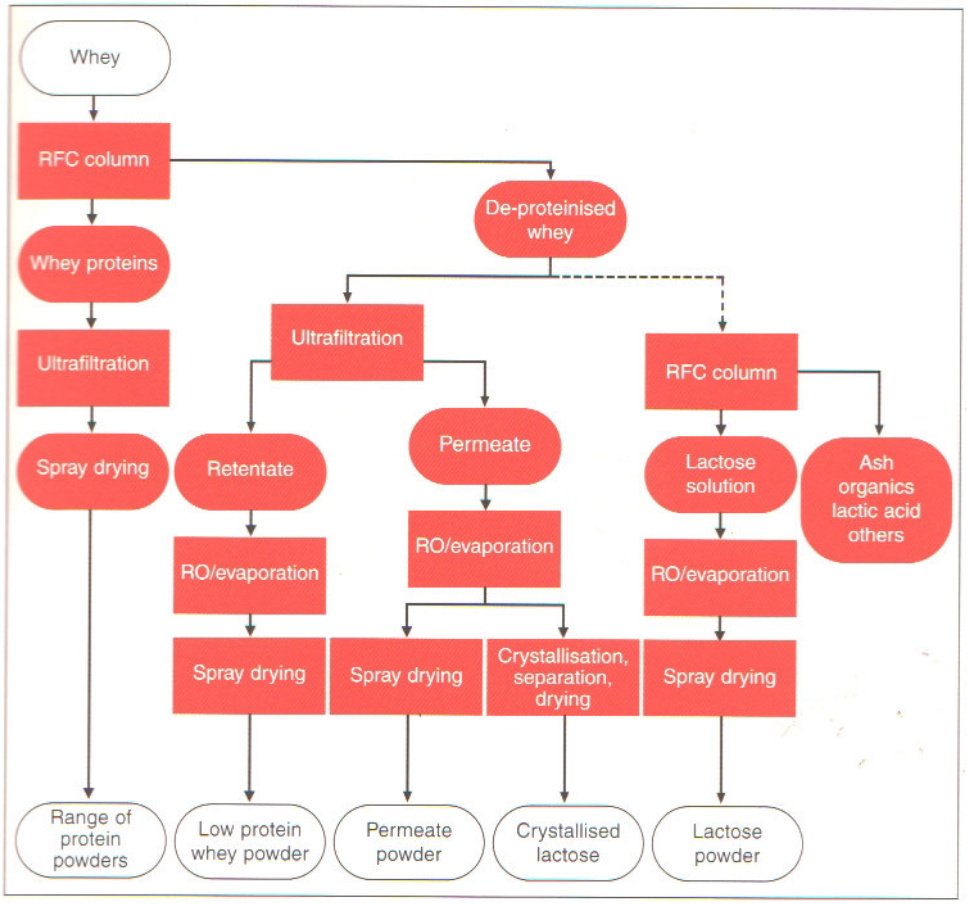
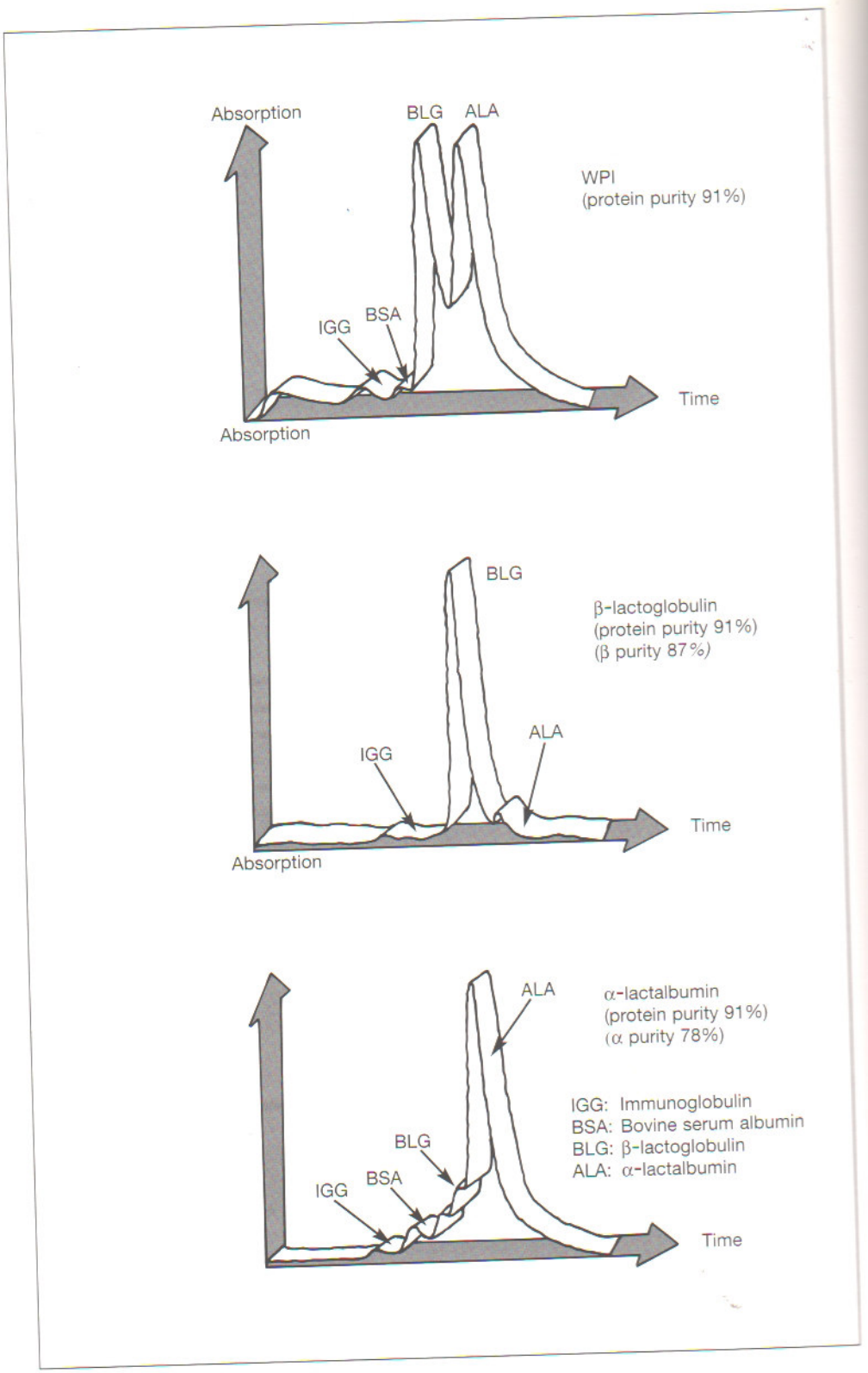


Figure 129: An RFC process. Through an intelligent combination of a variety of separation processes, it is possible to manufacture pure α-lactalbumin and β-lactoglobulin or pure isolated whey proteins.

Figure 130: Composition of whey protein samples. A total protein content in the powder of 91-94% and a purity of 78-96% of the individual proteins has been achieved using RFC.



		WPC35	WPC80	WPI
Annual powder production	'000 kgs	4,752	1,812	1,439
Estimated world market price	US$/kg	2.20	5.50	11.00
Total production costs	US$/kg	0.66	1.25	4.00

The data are based on a daily whey intake of 800,000 litres. The production costs include investment in equipment and machinery, and include all costs from whey pre-treatment to final powder in the bag

Table 39: Cost comparison for production of WPC and WPI.

Table 39 gives a comparison between the production costs of two types of WPC and WPI. For comparison, the estimated world market prices for the same products are stated.

The production of WPI and IWP opens up for a new range of opportunities.

The use of whey proteins to replace egg white proteins is a major breakthrough for applications in the bakery, candy and confectionery industries.

In the long run, there is a possibility of producing baby food milk replacer with a composition very close to that of human milk, which may be an important development.

Table 40 summarises the composition of milk from humans and cows. Even though the total content of whey proteins is almost the same in the two types of milk, there are substantial differences in the composition of the whey proteins. Human milk contains more α-lactalbumin and lactoferrin, while the content of β-lactoglobulin is negligible. This is where chromatography becomes important, due to its ability to isolate the individual proteins in a relatively pure form.

In the rapidly growing beverage industry, the proteins may be used in the formulation of highly nutritional soft drinks, making it possible to combine indulgence with health and providing valuable amino acids to the consumers.

Component	Human milk		Cow's milk	
	g/100 ml	% of whey protein	g/100 ml	% of whey protein
Total protein	0.95		3.30	
Casein	0.25		2.6	
Whey proteins	0.70	100	0.67	100
α-lactalbumin	0.26	37	0.12	18
β-lactoglobulin	-	-	0.30	45
lactoferrin	0.17	24	trace	
serum albumin	0.06	7	0.03	4
lysozyme	0.05	7	trace	
immunoglobulin	0.105	15	0.066	10
others	0.07	10	0.15	23
Total NPN	0.50		0.28	

Table 40: Comparison of the composition of proteins in milk from humans and cows.

Fruit juice

In the fruit juice industry, competition is tough, and the industry is constantly on the lookout for ways to reduce processing costs and new ideas that can lead to innovations for the benefit of the industry and consumers alike.

The technology used for whey protein separation has been tested in the citrus fruit industry in an attempt to develop a process to de-bitter citrus fruit juice. Experiments have shown that this process is very effective especially for companies which utilise only the first squeeze from their oranges or grape fruit. Juice drinks, which currently require the use of sweeteners, are obvious candidates for this new and simple de-bittering process.

Environmental applications

The current conventional chromatography techniques are cost-prohibitive for large-scale environmental separations. Radial flow chromatography has been tested in a number of different applications for removal of contaminants from waste water streams and, more recently, has also proven effective for removal of heavy metals from industrial fluids.

While other methods, particularly ion exchange and precipitation, are commonly used for heavy metal removal, radial flow chromatography has now proven to be very effective in removing contaminants like chlorinated hydrocarbons and heavy metals from waste water, down to the ppb range. The columns containing contaminants can either be regenerated on site, or transported to a common site for regeneration and back to the site of contamination for reuse.

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16 Economics of membrane filtration

This chapter is intended as a very broad overview of the economics of membrane filtration processes. Generally speaking, membrane systems are an expensive investment compared with alternative and more conventional processing systems. However, during the brief history of this technology there has been a remarkable development in pricing.

Within a few years at the end of the 1980s, prices dropped to about 35-50% of the original price level for plants in the food and dairy industries. This was very much a result of the spiral-wound membranes being widely accepted in the dairy industry, as the quality of the elements, especially from a sanitary point of view, was improved.

At the same time, spiral-wound elements became a competitive commodity with several manufacturers in the market.

The design and engineering of plants was simplified and standardised, which helped reduce the price level. However, despite the reduced prices, it is still important to view membranes as an investment in added value, new benefits, new products, lower energy consumption, less corrosion, etc. When these benefits are capitalised, they should outweigh the added cost of investment.

Capital costs

The investment cost in a membrane plant depends on several factors such as plant size, application and industry, level of automation and process design. The most dominant factor, however, is the selection of the membrane system. As previously described, each of the membrane systems has its specific advantages and disadvantages, and the selection of the membrane system must be made with this in mind.

Membrane system	Investment price US$/m^2
Spiral-wound	150-600[1]
Tubular	1,000-1,500[2]
Plate-and-frame	1,500-5,000[3]
Hollow fibre	1,500-2,000
Ceramics	5,000-15,000[4]

[1] US$ 300 for 1,000 m^2 plants
[2] US$ 1,500 for 400-500 m^2 plants
[3] US$ 5,000 for 20-40 m^2 plants
[4] US$ 10,000 for 50-75 m^2

The prices are average figures based on complete, continuous, multi-stage, fully automated plants in a sanitary design

Table 41: Investment price levels for typical membrane filtration systems.

Table 41 gives a very general indication of the price level for the most common membrane systems. The prices include the complete operational membrane system from balance tank inlet to permeate and concentrate outlet. However, the price per installed m^2 membrane area cannot be used directly to compare the different systems, as the performance (flux) of the individual membranes varies greatly.

Spiral-wound systems have for many years been the least expensive per m^2 membrane area. Due to the severe competition, the prices are now at a level

where it is unlikely that there will be further significant reductions. The average flux rate for UF spirals for a typical application like whey/skimmilk protein concentration is normally in the range of 10-50 lmh.

Tubular systems are more expensive than the spiral-wound systems but it should be kept in mind that tubular systems can handle fluids containing particles which would block a spiral-wound system. There are a few low-priced tubular systems on the market, selling at a price level similar to that of spiral-wound systems, but they have some severe temperature and pressure limitations and can only be used for special undemanding applications.

The average flux rate for apple juice clarification using tubular UF membranes is typically around 150 lmh.

Plate-and-frame systems are considerably more expensive than tubular systems. The plate-and-frame system is used in areas where its ability to handle high-viscosity products can be utilised, e.g. in the pharmaceutical industry and for certain applications in the food and dairy industries.

A UF quarg/Cream cheese process using the plate-and-frame system typically performs at an average flux of 20-50 lmh.

Hollow fibre systems are on a price level similar to that of the tubular systems. They have not changed much in recent years and the elements are similar to the original design.

A typical hollow fibre application is UF for electrophoretic paint recovery, which performs at an average flux in the range of 30-50 lmh.

Ceramic systems are known for their high price level. This, however, should be seen in the light of their unique properties in terms of chemical and temperature stability, very long membrane lifetime, back flush capability and membrane selectivity - especially in the MF range. Ceramic membranes are new on the market compared with organic membranes, and it is expected that new concepts and new manufacturers will appear, thus increasing competition.

Moreover, ceramic membranes can be tuned to perform very high fluxes - for instance 500-700 lmh for MF skimmilk applications.

All membrane systems are modular in their basic design, and this means that for large continuous systems there is almost proportionality between membrane area and investment cost.

Different industries have different standards for plant design and different regulatory requirements, and a distinction should be made between the following areas:

- Sanitary design
  - pharmaceutical
  - dairy, food and beverage
- Non-sanitary design
  - industrial
  - water treatment

The non-sanitary design is less expensive to manufacture and the components used are also normally less expensive. For water treatment systems, the construction materials are often PVC or other plastics. The water treatment area is very competitive especially for large volume plants.

The price levels stated above refer to sanitary systems. In most cases, the requirements in the pharmaceutical industry are higher, due to validation requirements, surface finish, etc.

The system design and level of automation also plays a major role in the price

level. Batch systems, which are manually operated, are naturally less expensive than continuous, multi-stage fully-automated systems. The so-called Christmas tree design (cp. Figure 64), a continuous system without recycling, is used for many water treatment systems and is less expensive in investment than the continuous multi-stage plant.

Membrane replacement costs

Table 42 summarises the membrane replacement costs for different systems. *Spiral-wound systems* are clearly very competitive. It is also the type of system requiring the least amount of labour for replacement, which reduces labour costs and, perhaps more importantly, reduces down time during membrane replacement.

The gap from 30 to 80 US$ per m^2 relates to element type and application. The low price reflects the commodity market for large volumes of 8.5-inch elements containing up to 50 m^2 membrane area, and the high price reflects the market for small, more specialised elements with increased spacer and higher flow channel.

Tubular membranes require more labour in manufacturing, which contributes to the higher price. Furthermore, the volume is much lower than for spiral-wound membranes, which also contributes to the higher price.

The plate-and-frame replacement costs are relatively high, but should be seen in relation to a relatively low equipment sales volume, a low membrane utilisation (approximately 50% of the 'raw membrane' goes to waste due to the shape), and a price policy positioning plate-and-frame as the 'Rolls Royce' model. In addition to the price of membranes, there is a relatively high labour cost and an ongoing exchange of the plastic support plates, which have a limited lifetime.

Membrane system	Replacement costs US$/m^2
Spiral-wound	30-80
Tubular	100-120
Plate-and-frame	110-160
Hollow fibre	300-700
Ceramics	2,000-2,500

Table 42: Membrane replacement costs for typical membrane systems.

The hollow fibre system has an even higher price for membrane replacement which, taken with other limitations, makes it difficult to justify this system for many applications.

Finally, *ceramic membranes* are the most expensive system of all, as far as replacement costs are concerned. As already mentioned, there is reason to believe that the general price level may fall in the future. Moreover, the membranes last for a very long time, compared to ordinary organic membranes, and this diminishes the significance of the high replacement price.

Cleaning costs

Cleaning of molecular separation systems is essential for their successful operation. Plants handling food, dairy or beverage products generally need to be cleaned every 20 hours or sometimes even more frequently. In the industrial sectors, and for water treatment, such frequent cleaning may not be required but it is still essential that a well-documented cleaning procedure exists.

Because membranes and resins are usually made from polymers, efficient cleaning is more tricky than if the entire plant was made from steel. This has caused the suppliers of formulated cleaning chemi-

Table 43: Comparative cleaning costs for spiral-wound and tubular RO whey concentration plants with TFC membranes.

	Plant 1 (spiral-wound)		Plant 2 (tubular)	
	Quantity	US$/day	Quantity	US$/day
Dead volume	1,100 litres		2,120 litres	
Water flushing	16.5 m^3	23	15 m^3	22
Acid cleaning	3.3 kg	5	6.4 kg	9
Caustic cleaning	17.6 kg	32	34 kg	63
Disinfection	6.6 kg	15	11 kg	25
Total		75		119

Plant 1: Spiral RO plant, 30 mil spacer, whey concentration from 5.5 to 15% TS, 15,000 kg/h permeate, thin film composite membranes

Plant 2: Tubular RO plant, ½-inch diameter tubes, whey concentration from 5.5 to 15% TS, 15,000 kg/h permeate, thin film composite membranes

cals around the world to take an interest in formulating special cleaning agents for specific membranes and resins.

Today, the membrane manufacturer or the supplier of the complete membrane system will normally recommend a range of different cleaning procedures for a user to choose between. It is strongly recommended to follow the advice given by the manufacturers, and doing so will always be a condition for the membrane warranty where such a warranty is given.

The cost of cleaning the system is an important part of the total operating costs of a plant. Since cleaning requires a certain concentration of the cleaning agent, the actual consumption depends on the dead volume in the plant. Consequently, a tubular system with ½-inch membranes is more expensive to clean than a spiral-wound system with a 30 mil spacer.

Table 43 compares the cleaning costs for such two systems. The dead volume in the tubular system is almost twice that of the spiral-wound system, giving a 55% overall increase in the cleaning costs.

The added costs must be seen in relation to the added benefits of the tubular system, which is able to handle liquids containing fibres and particles up to a certain size.

Energy consumption

The different types of molecular separation processes need energy for the required performance.

Figure 5 (see Chapter 3), illustrates how the various processes are driven by different types of driving forces. Naturally, the energy consumption is most important in the pressure and electricity driven processes. For the resin-based processes, the energy consumption relates only to the transfer of liquids and to the necessary heating and cooling.

The theoretical energy consumption can easily be calculated when the operating pressure for a pressure-driven process is known. However, the operating pressure accounts for only part of the total energy consumption.

Plant 2 (tubular)

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In cross-flow based processes, a considerable amount of the energy is consumed by the recycling pumps installed to continuously flush the membrane, keep the membrane surface clean and minimise the effects of concentration polarisation. The power consumption for each pump in a system can be estimated in the following way:

$$\text{Power consumption (kW)} = \frac{\text{Flow (m}^3\text{/h)} \times \text{Pressure increase (bar)}}{\eta \times 36}$$

η = pump and motor efficiency
η = 0.85 for positive pumps
η = 0.65 for efficient centrifugal pumps

For conversion of sea water to drinking water, a minimum pressure of 70 bar is required and the water utilisation would be 33% as a maximum, depending on the salinity of the feed. According to the formula above, the energy consumption can be calculated as:

$$\text{Energy consumption (kWh/m}^3\text{)} = \frac{\text{Pressure (bar)}}{\eta \times 36 \times \alpha}$$

α = water recovery (the fraction of feed converted to permeate)

$$\text{(kWh/m}^3\text{)} = \frac{70}{0.65 \times 36 \times 0.33} = 9.1$$

Normally, the energy consumption for converting sea water to drinking water is in the range of 9-12 kW/m³. For large sea water desalination plants it is common practice to use energy recovery turbines to recover the large amount of energy in the concentrate. Using energy recovery systems will reduce the energy consumption to 6-8 kWh/m³. In comparison, desalination by means of vapour-compression based evaporation or multi-stage-flash distillation, would require 12-18 kWh/m³.

Process type (cross-flow)	Energy consumption kWh/m³ permeate
Microfiltration	9-12
Ultrafiltration	2-5
Nanofiltration	4-6
Reverse osmosis	5-10

Table 44: Energy consumption for pressure-driven membrane processes.

For a brackish water desalination plant, the same calculation would result in an energy consumption of 2.5-3.5 kWh/m³ for an RO plant treating brackish water with a salinity of 3,500 ppm and 65% water recovery. Using ED for desalination of the same water type for production of drinking water quality would require an energy consumption of 4-6 kWh/m³.

The energy input from the pumps can contribute to a significant heating of the treated product which is not always acceptable and consequently the product must be cooled during operation. Table 44 shows the energy consumption for the four most common pressure-driven processes.

Despite the fact that RO operates at high pressures, the energy consumption is not as high as for MF, in which a lot of energy is needed to keep the membrane surface clean by a high flow rate.

The pressure-driven processes require some energy for operation, but compared with the thermally based phase change processes the consumption is very low.

Processing costs comparison

In order to justify a particular application for a molecular separation process, it will normally be required to calculate the actual cost of using the process, and

compare it with a more conventional alternative or with other molecular separation processes.

On the basis of the principles outlined in the previous sections, both the operating costs and the capital costs can be estimated. This section presents some examples of such cost calculations and cost comparisons.

Desalination of water

Desalination of sea and brackish water using RO can be calculated on the basis presented in the previous section. Table 45 summarises the calculations for typical sea and brackish water. The sea water calculation is based on desalination in one step only.

In very rough terms, the cost of producing fresh water from brackish water will vary between 0.35 and 0.65 US$/m^3 and for desalination of sea water between 0.7 and 1.4 US$/m^3 in both cases depending on cost of energy, feed water salt content, temperature, requirements for pretreatment, etc.

Even though the investment in RO plants is high, the figures illustrate that water desalination is a process which can be applied generally at an affordable cost for both sea and brackish water.

Concentration of whey

Concentration of whey is a typical example of an area in which RO competes with evaporation. As described in Chapter 14, many improvements in evaporator design and operation have been made in recent years. A comparison is always difficult to make, since it depends on local circumstances such as space requirements, existing building facilities, local cost of energy, future expansion, etc.

Table 46 compares the costs of whey concentration using either an evaporator or an RO/evaporator combination. The plant concentrates 15,000 litres of whey per hour from 5.5 to 33% TS, prior to transportation to a central whey treatment facility. In the first case, the whey is concentrated only by means of an evaporator, while in the second case, the bulk of the water is removed by means

Table 45: Comparative costs of water production from brackish and sea water desalination with RO.

	Brackish water		Sea water	
	US$/m^3	%	US$/m^3	%
Chemicals				
Sulphuric acid	0.01	2.0	0.06	8.0
Polyphosphates	0.02	6.0		
Membranes	0.03	7.0	0.13	17.3
Energy	0.26	71.4	0.44	58.7
Total variable costs	0.32	86.4	0.63	84.0
Depreciation	0.05	13.6	0.12	16.0
Total costs	0.37	100.0	0.75	100.0

Basis:
Cost of energy: 0.08 US$/kWh
Cost of membranes: 50 US$/m^2, 3 years lifetime
Plant capacity: >2,000 m^3/day
Flux: 33 lmh for sea water
Flux: 75 lmh for brackish water
Cost of equipment: 350 US$/m^2 membrane area
Years of depreciation: 10

	US$/day			
	5.5-15% RO	13-33% TVR	RO & TVR	33% MVR
Membranes	90		90	
Power	163	72	235	551
Cooling	98	10	109	21
Heating	22	141	163	81
Cleaning	67	59	126	76
Total	441	282	722	729
Permeate/condensate m³	362	125	488	488
Costs in US$/m³	1.22	2.25	1.48	1.49

Feed: 30,000 kg/h, 6% TS
Concentrate: 5,625 kg/h, 32% TS
Permeate: 18,101 + 6,274 kg/h

Table 46: Comparative costs of whey concentration using an evaporator or an RO/evaporator combination.

of RO. The RO plant concentrates the whey from 5,5 to 15.0% TS, prior to final evaporation to 33.0% TS.

The calculation reveals that for a new installation, there is a marginal advantage in using the combination of RO and evaporation. However, where an existing evaporator needs to be extended, it may often be possible to make the extension with RO at a considerably lower cost than rebuilding or extending the evaporator.

It should also be taken into consideration that the RO system is easy to install and to extend to larger capacities, due to its modular design. The flexible nature of an RO system may often be a decisive factor when the final choice of equipment is made.

As mentioned in Chapter 14, the use of NF for whey concentration gives the additional advantage of removal of salts. In cases where such salt removal is beneficial to a point where it can be capitalised, there is one more reason to use membrane filtration for the initial concentration step.

	Ultra-filtration US$/m³	Traditional US$/m³
Operating costs		
Power consumption	0.81	0.08
Membranes	0.17	
Chemicals	0.04	0.30
Manpower	0.30	3.60
Capital costs		
Interest for UF	0.25	
Interest for vinegar store		0.28
Total costs	1.57	4.26

Basis:
- Annual capacity: 10,000 m³ vinegar
- Membrane flux: 100 lmh
- UF plant size: 18 m² membrane area
- Plant load: 250 days/year, 22 hours/day
- UF plant investment: US$ 49,500 (excluding membranes)
- Interest rate: 10%

Annual savings using UF: USD 26,900
Repayment of investment: <2 years

Table 47: Comparative costs of a traditional and a UF-based vinegar production.

Vinegar purification

The production of vinegar using UF for the final clarification was illustrated in Figure 106, (see Chapter 14). The UF process eliminates the need for 3 to 6 months' storage of the vinegar, prior to final clarification.

Vinegar plants are relatively small and Table 47 shows the operating costs for a plant with an annual capacity of 10,000 m^3. The reduction in operating cost is very much related to the saving in manpower and chemicals. This saving justifies the investment in a fairly expensive UF plant, with a repayment period of less than 2 years.

This is an example of how even small operations can provide clear financial justifications for applying molecular separation processes.

17 Intelligent combinations of molecular separation processes

Molecular separation processes are normally used individually and fulfil a purpose in their own right. Desalination of sea water with RO is a typical example. In many cases, however, the combination of a range of separation processes improves the process and minimises the operating costs.

Consequently, it is relevant to speak of 'intelligent' combinations of molecular separation processes where the processes may complement each other in a way not seen before.

Also the rapid development in automation and the use of PC-based intelligent automation systems enhance the opportunities for new process development in this area. This is probably just the beginning of a new era where a large number of new opportunities will surface. The following sections illustrate a few of these new opportunities.

Water treatment

One of the challenges in sea water desalination is the pre-treatment of the feed prior to RO. The conventional pre-treatment consists of sand filter, chlorination and de-chlorination, safety filtration, pH adjustment and addition of antiscaling agents. Using UF/MF as an alternative to the conventional pre-treatment shows very promising results, giving a higher and more stable flux rate for the RO plant.

In the production of drinking water from surface water, the traditional treatment is

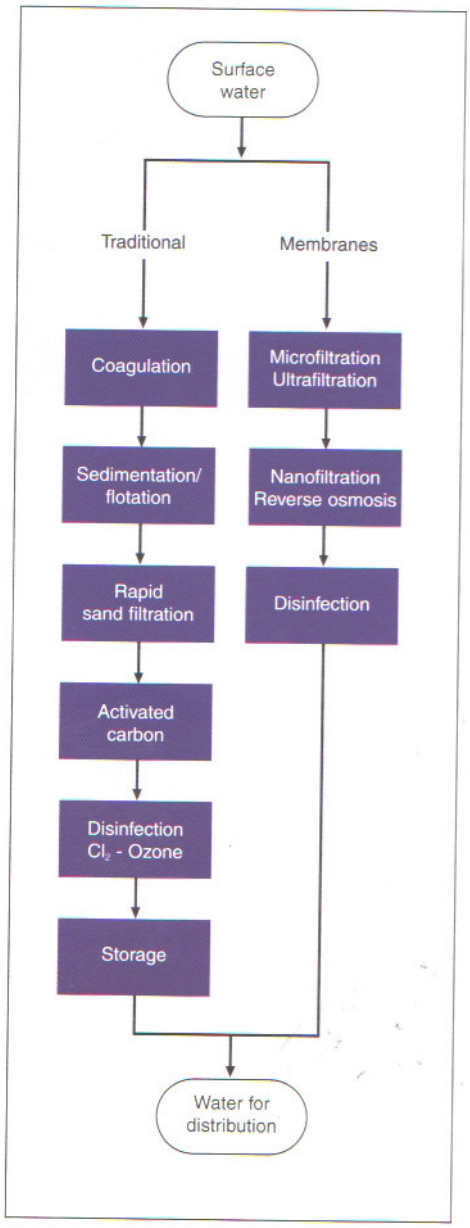

Figure 131: Alternative treatment of surface water. Using UF/MF instead of the traditional water treatment may provide improved water quality.

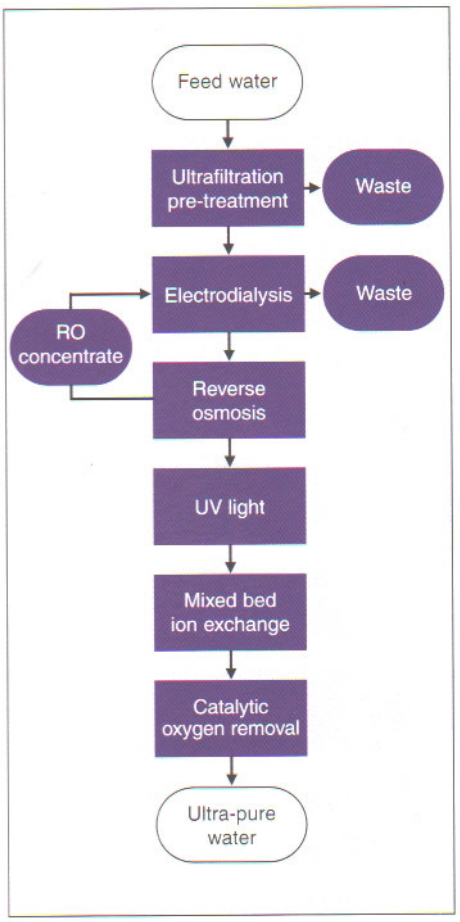

Figure 132: Production of ultra-pure water using a combination of molecular separation processes. Using UF as a pre-treatment method for ED, combined with RO and mixed-bed ion exchange, provides a superior, ultra-pure water quality.

coagulation, sedimentation, sand filtration, activated carbon treatment and disinfection. Figure 131 illustrates how UF/MF followed by NF/RO can do the same job. The membrane processes may even produce a better quality of water by removing organic compounds not captured by the traditional processes.

Production of ultra-pure water depends on the quality of the raw water, both in terms of the content of fouling material (colloids, organic material) and the salt content. Figure 132 illustrates how UF can be used as a pre-treatment of the feed water for an ED plant removing a large portion of the salts. The product water from the ED plant is treated by RO, then by UV light, followed by mixed-bed ion exchange for removal of the last traces of salts. Finally, the water goes through a catalytic oxygen removal system, where the oxygen content is reduced to a few ppb.

Whey treatment

Many of the possible process combinations were dealt with in the section on dairy applications in Chapter 14. Since many of the processes benefit from a concentration of the whey prior to further processing, NF can be seen as a universal first-step treatment concentrating the whey and simultaneously removing some of the undesirable sodium chloride. This improves the economy in the subsequent electrodialysis or ion exchange steps for the production of demineralised whey.

In the section on chromatography in Chapter 15, the possibilities for production of IWP or WPI were described. Chromatography requires a lot of water for eluation and flushing. The products come out of the column as diluted solutions, containing salts used for buffer and ion strength adjustments. By means of UF and diafiltration, it is possible to concentrate the proteins and at the same time regenerate the water and the buffer salts, thus improving the total economy of the process. Prior to reuse, the recovered buffer solution is concentrated by RO before it is returned to the eluation tank.

The use of intelligent automation facilitates the combination of the various process steps and it is almost indispensable in the control and operation of the chromatography column. Careful timing and control of the various steps is essential for the optimisation of the yield of the various protein fractions and minimisation of the waste from the plant.

Additionally, membrane processes may be used both in the production of lactose

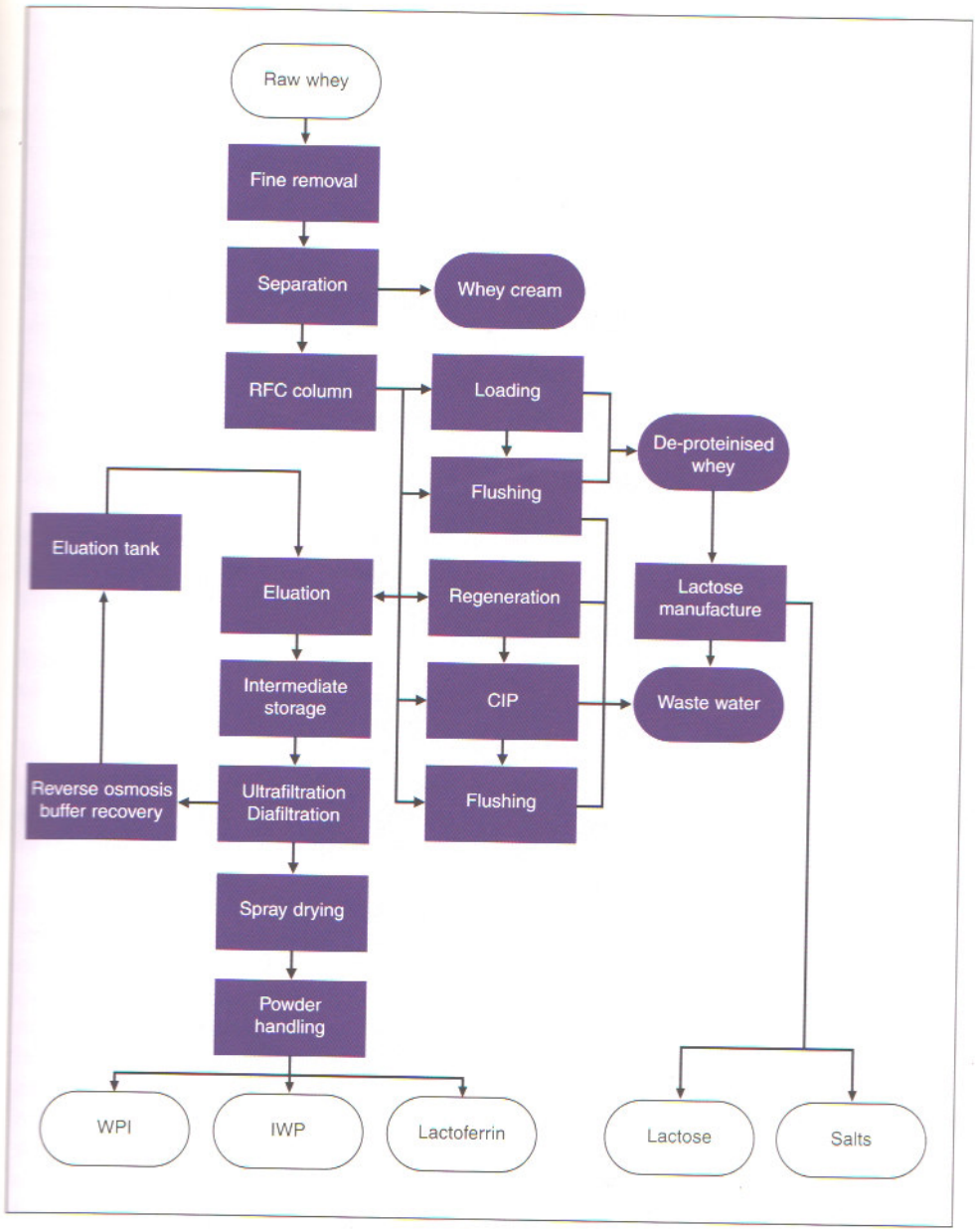

Figure 133: Production of WPI and IWP by an intelligent combination of industrial molecular separation processes. Chromatography provides excellent protein separation, while the membrane processes concentrate and purify the fractions.

and in the further treatment of the generated waste water.

The process is illustrated in Figure 133, and includes RFC, UF, RO/NF, centrifugal separation, evaporation, crystallisation and drying. In truth, a revealing example of the intelligent combination of different separation processes.

18 What the future may bring

During the past 20-40 years, the spectrum of molecular separation processes has gone through a phase of exciting development.

New products have been brought onto the market, new and effective ways to produce fresh water have contributed to improved living conditions for mankind and, maybe most important of all, new cost effective ways have been established to solve the growing problems of environmental pollution.

But what will the future bring in the area of molecular separation processes?

First of all, the business is expected to grow at an annual rate of 5-7% in general and this is a quite healthy growth rate in the industrial equipment business.

Secondly, it should be kept in mind that the development of new separation processes takes time. Sometimes people express disappointment that the development in specific separation processes has been slower than predicted. Looking back, however, the development has been rapid, but of course there are bound to be some disappointments and hiccups, mixed with the successes. As illustrated in this book, there have been many successes and there will be many more to come.

The following headings illustrate what molecular separation processes have given us:

- *Manufacture of new products*
  - the production of Cast Feta cheese
  - the production of WPC, WPI and IWP
  - the production of MPC
- *Product quality improvement and added value*
  - for water purification, ultra-pure water, de-ionised water
  - from removal of bacteria and spores from milk
  - for production of low-alcohol beer
- *Improved production economy*
  - lower costs for the production of drinking water from saline water
  - lower costs and improved yields in the manufacture of enzymes and antibiotics
  - lower costs in the production of pure alcohol from fermentation
- *Solution of environmental problems*
  - the recovery of electrophoretic paint
  - the recovery of heavy metals and volatile organic compounds
  - water and product recovery in the food industry

Future developments will come under the same headings. The solution to environmental problems is much in line with the very nature of molecular separation processes:

'Separating components at the molecular level and bringing them back to where they belong'

The following areas are seen as major issues influencing the development of molecular separation processes in the future:

- *Hybrid processing*
  - combining different separation processes opens up new opportunities. It will be more common for separa-

tion companies to provide service over a range of processes and supply total solutions to separation problems

- *Intelligent systems*
  - the concept of intelligent systems and plants will assist the development of molecular separation processes which are often seen as complicated and risky to use. Adding more intelligence to the operation will make users more confident and eliminate the risk of disasters, such as destroying a set of membranes or resins. The intelligent combination of processes will become more sophisticated, and will promote the use of the most appropriate separation technology

- *Unit operation*
  - just as membranes are seen as conventional unit operations in water desalination and in the dairy industry, they will spread to other industries as their power is realised. This could be the case for the brewing industry, if a suitable process can be developed for main stream beer filtration

- *Reduction in use of chemicals*
  - there is an increasing trend to avoid chemicals in the processing of food and beverages in order to produce more healthy and natural products. As illustrated in Chapter 14, the molecular separation processes are in many cases able to reduce or even eliminate the use of chemicals

- *Price structure*
  - the price structure of membranes, membrane modules, resins and columns is a major factor in determining the industrial use of membranes and chromatographic resins. As an example, the cost of ceramic membranes limits their applications, and a real breakthrough will only happen when the price level has been brought down. This is also the case for chromatographic resins, which so far have been used mainly for products which can justify the very high cost

Based on these trends, we could expect that the beer we drink in the future is filtered by MF without any use of kieselguhr. The milk we need could be filtered by MF, at the same time removing impurities, bacteria and spores. The wine we enjoy could be manufactured ecologically and simply, by reducing the need for SO_2 addition.

Water and air should become cleaner to drink and breathe and the amount of waste should be reduced because of recycling.

New products like humanised baby food will appear on the market, and molecular separation processes will play a significant role in the development and production of new drugs and other pharmaceutical products.

Molecular separation processes have come a long way already in a relatively short time, and there is good reason to believe that the future will become even more exciting than the past.

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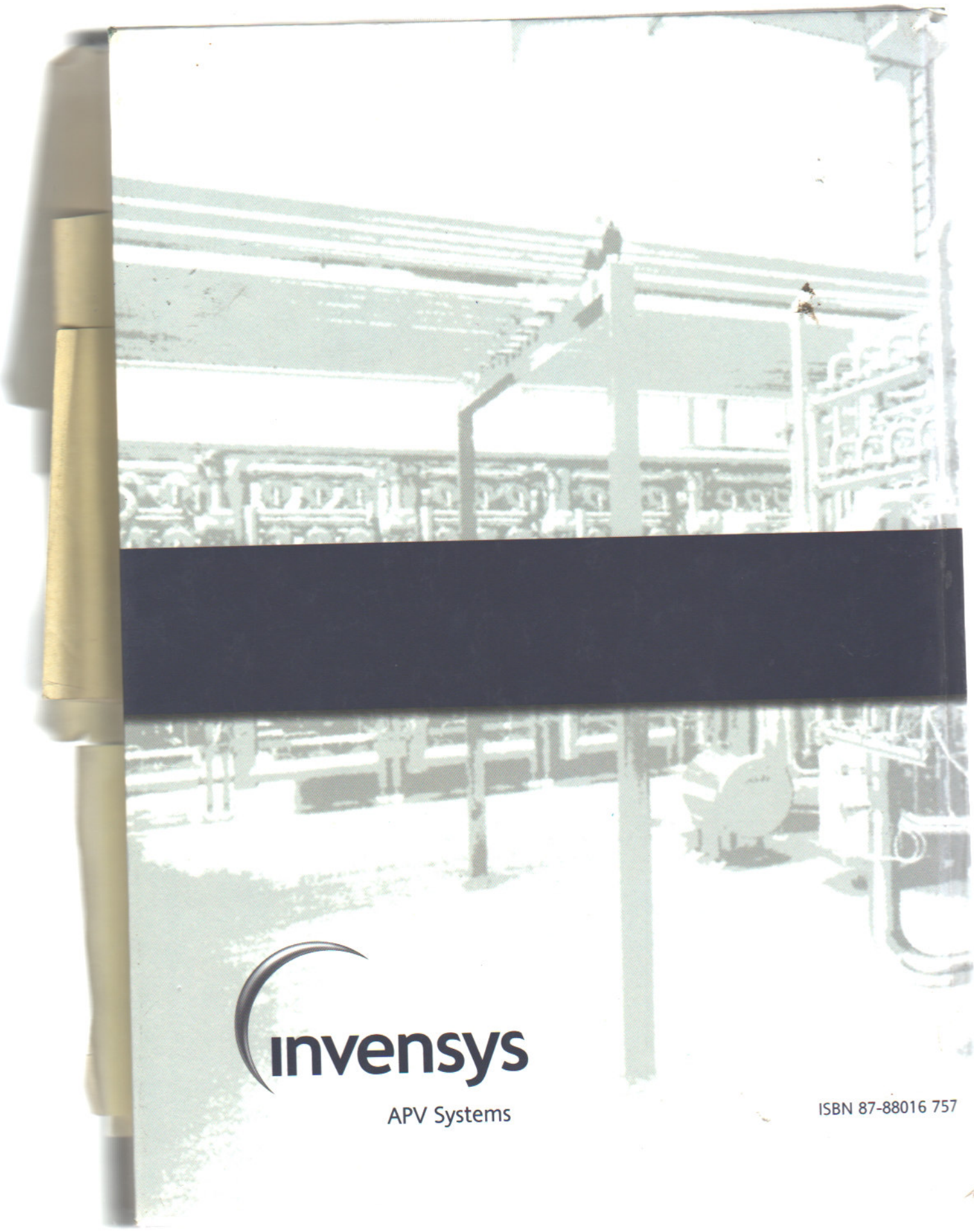

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