CHAPTER 8

Membranes

In filtration terms, membranes started as thin, flexible semi-permeable sheets of regenerated cellulose material, developed to separate species at the molecular and ionic level, their first main application being in the purification of salt and brackish waters by reverse osmosis. The word 'membrane' has stuck to a range of filter media that has expanded enormously from this early form, to embrace solid inflexible ceramic and sintered metal, and an ever-increasing group of polymeric materials, and to applications that now extend well into the microfiltration range. The existence of the membrane as a very effective filtration medium led to the development of the whole field of cross-flow filtration, which also now extends well beyond its reverse osmosis origins.

This chapter provides an introduction to the membrane as a filter medium, but makes no attempt to be a complete reference on membranes, even in filtration, let alone their wider uses. There is here a good deal of information about the ways in which membrane systems are used, but only enough to set the membrane media themselves in context. For a more complete reference to membranes of all kinds, the reader is directed to Keith Scott's *Handbook of Industrial Membranes*[1], on which the corresponding chapter of the first edition of this Handbook was largely based.

8.1 Introduction

The first edition of this Handbook defined membranes as follows:
'A membrane is a thin sheet of material which exhibits some degree of permeability to fluids thereby permitting phase or species separations to be affected for particles in the size range from a few microns down to molecules.'

Any attempt now to provide a succinct but comprehensive definition of a membrane is very much complicated by the immense and ever-growing diversity of membranes available, by the variety of mechanisms by which they function, and by the multiplicity of applications for which they are used. To many people, a membrane remains a thin flexible material, but in filtration terms the term now

covers any medium that can achieve separations at 0.1 μm or below (down to molecular and ionic sizes), and which may be thick or thin, flexible or rigid, organic or inorganic. Many membranes are now employed in microfiltration applications at cut sizes well above 0.1 μm.

The membrane is essentially a surface filtration device, with little or no depth filtration involved in its use. In practice, many membranes are of asymmetric structure and effectively comprise two layers. The active, surface layer is a very thin skin, the permeability of which is of critical importance. The lower, thicker layer is of more open structure, its role being to serve as a mechanical support for the active layer.

This chapter looks firstly at the way membranes are used in filtration applications, and then at the nature of membrane media, and the ways in which they are made. A brief look at membrane characterization is followed by a review of some typical membrane media available on the market, and some guidance as to their selection. It is primarily concerned with the use of membranes in particulate separations, i.e. in microfiltration, but membrane media are now used in such a wide spectrum of applications, with considerable overlap among what were once clearly separate uses, that these other applications are covered here as well.

The membrane represents probably the fastest growing part of the filtration media market (especially if ceramic membranes for hot gas filtration are included). The most important of the changes in the membrane business since the first edition of this Handbook are:

- the extension of membrane media into microfiltration applications;
- the growth in importance of expanded PTFE as a membrane material;
- a corresponding growth of ceramic materials for membranes; and
- the development of techniques for the increase of stabilised fluid flux by the disturbance of boundary layers at the membrane surface.

8.2 Membrane Systems

In order to gain a good grasp of the nature and use of filtration membranes it is first necessary to look at the way in which membranes are used, both in process terms, and in their actual structural format. The fine surface structure of all membranes implies the need for significant pressure drops across the medium in order to achieve adequate fluid fluxes. As a result, membranes need to be contained in pressure-tight housings, and considerable ingenuity is required of the suppliers to achieve sound and efficient operation.

8.2.1 Membrane processes

Historically, membranes were first developed to work at the lowest size levels of separation, the removal of salts, i.e. ionic species, from water at quite high flow rates to produce water of drinkable quality. This application required high working pressures, but over the subsequent years the membranes have become 'looser', and the pressures required have become less, as the membrane has

been used for separations at progressively higher sizes – because membranes have decreased in cost, and so become attractive for an increasingly wide range of applications. The broad spectrum of membrane processes is illustrated in Figure 8.1.

The highest levels of permeability correspond to membranes of relatively coarse microporous structure that permit the transmission of liquids that can be solutions of macromolecules; they reject fine suspended solids down to less than 0.1 μm by *microfiltration* at relatively low differential pressures (1–4 bar). Less permeable membranes, of finer microporous structure, allow passage of solutions of smaller molecules and ions; functioning by *ultrafiltration* at differential pressures up to about 10 bar, they reject finer particles and molecules of molecular weight above about 10 000. Membranes in these two categories (microfiltration and ultrafiltration) are the main theme of this chapter.

Contrasting with these are the semi-permeable membranes of *reverse osmosis* (or hyperfiltration), the asymmetric structure of which incorporates a thin non-porous homogeneous skin; under pressures of 30–60 bar, these membranes are capable of the finest possible level of separation, including the rejection of dissolved salts, and the complete removal of bacteria, pyrogens and organics from water. *Nanofiltration* is essentially a form of reverse osmosis operating at pressures in the range 20–40 bar, using a 'looser' membrane so as to restrict rejection to molecules in the molecular weight range 300–1000, and to larger ions (such as Ca^{2+} and Mg^{2+}), and the very finest particles.

These four specifically liquid filtration-related membrane processes are shown in Figure 8.2, with main applications for each. It should be noted that the separation size ranges overlap at each end.

Membranes incorporating thin layers of dense non-porous material utilize *gas permeation* to separate gases (such as hydrogen recovery from refinery exit streams, or the separation of oxygen and nitrogen from air), and *pervaporation* to separate miscible liquids, as an alternative to fractional distillation. Yet other mechanisms, utilizing electrically charged or ion exchange membranes, are involved in processes such as *electrodialysis*, and in fuel cells.

The full range of membrane processes is listed in Table 8.1, with typical membrane types, and associated driving forces and typical applications.

It should be noted that the use of the term 'non-porous' in the above definitions relates to the impossibility of the flow of fluids carrying particles through continuous open pores in the medium. Such materials are still permeable to molecular or ionic species by means of diffusion through the solid mass of the non-porous layer.

Because of the very fine nature of the membrane media, it is normal practice to employ a filter, ahead of the membrane unit, that is intended to remove any particulate material that might interfere with the membrane process. This is especially necessary where the flow passages are very narrow, such as in hollow fibre membranes. In fact, some membranes themselves are used as prefilters to membranes operating at a finer degree of separation. Thus there will normally be a microfilter ahead of an ultrafiltration or reverse osmosis membrane, but there may also be an ultrafiltration membrane ahead of a reverse osmosis step.
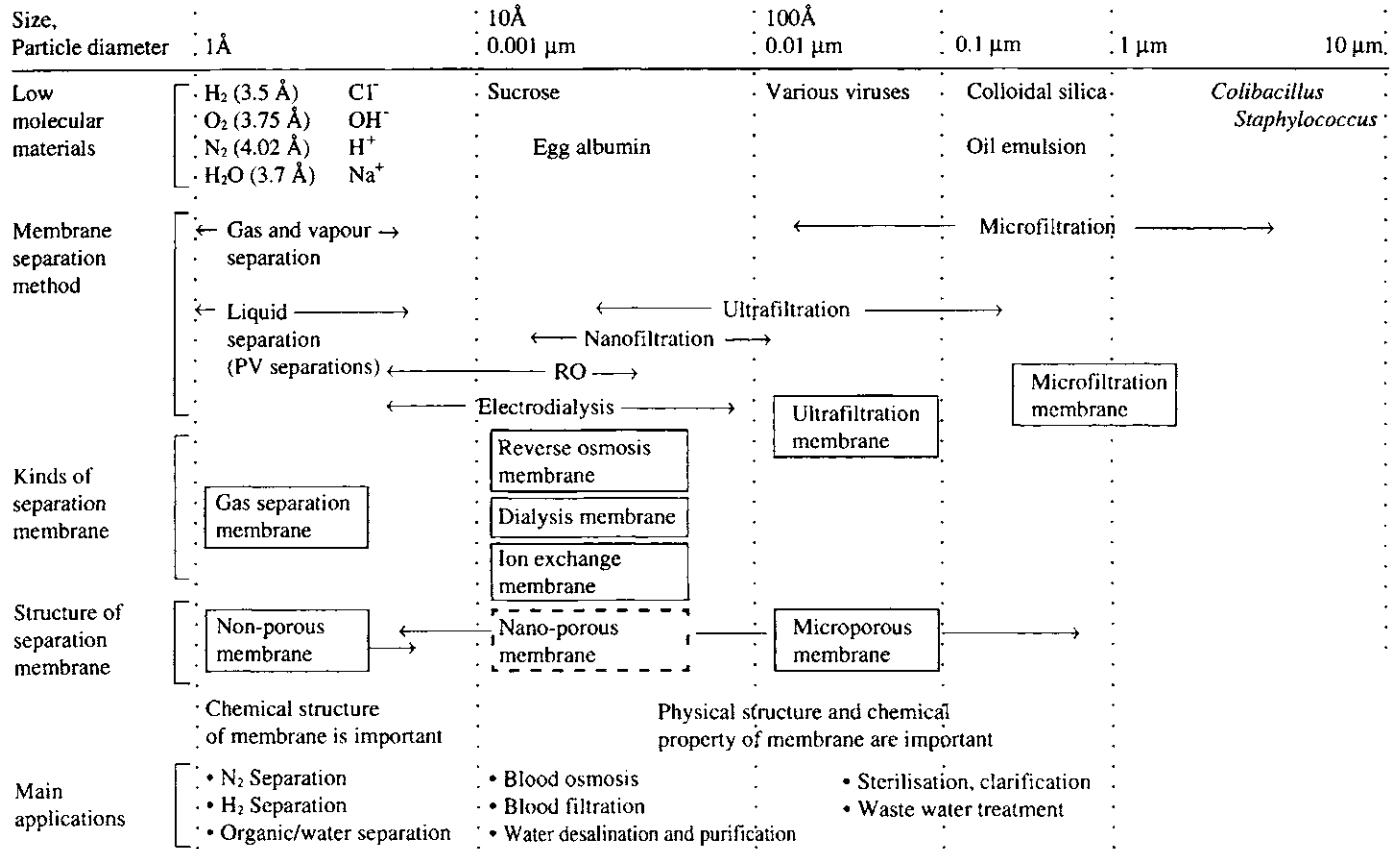
Size, Particle diameter	1Å	10Å 0.001 µm	100Å 0.01 µm	0.1 µm	1 µm	10 µm

Low molecular materials

H₂ (3.5 Å) Cl⁻	Sucrose	Various viruses	Colloidal silica		Colibacillus

- H₂ (3.5 Å) Cl⁻
- O₂ (3.75 Å) OH⁻
- N₂ (4.02 Å) H⁺
- H₂O (3.7 Å) Na⁺

Sucrose

Egg albumin

Various viruses

Colloidal silica

Oil emulsion

Colibacillus
Staphylococcus

Membrane separation method

← Gas and vapour → separation

← Microfiltration →

← Liquid → separation
(PV separations)

← Ultrafiltration →

← Nanofiltration →

← RO →

← Electrodialysis →

Kinds of separation membrane

Gas separation membrane

Reverse osmosis membrane

Dialysis membrane

Ion exchange membrane

Ultrafiltration membrane

Microfiltration membrane

Structure of separation membrane

Non-porous membrane → Nano-porous membrane → Microporous membrane

Chemical structure of membrane is important

Physical structure and chemical property of membrane are important

Main applications

- • N₂ Separation
- • H₂ Separation
- • Organic/water separation

- • Blood osmosis
- • Blood filtration
- • Water desalination and purification

- • Sterilisation, clarification
- • Waste water treatment

Figure 8.1. An overview of membrane separation technology.

REVERSE OSMOSIS

ULTRAFILTRATION

NANOFILTRATION

MICROFILTRATION

Aqueous Salt

Enzymes

Paint Pigment

Atomic Radius

Lignosulphonate

Yeast

Metal Ion

Synthetic Dye

Virus

Bacteria

Oil Emulsions

Wood Resin

Lanolin

Antibiotics

Gelatin

Lactose

Colloidal Silica

Blue Indigo Dye

Detergents

Egg Albumen

Flavours & Fragrances

Latex

Particulates

100	200	1,000	10,000	20,000	100,000	500,000	Approximate Molecular Weight
	0.001			0.01			Micrometers (logscale)

0   0.1   1.0

Pressure, bar   30-60   20-40   5-10   1-4

Applications

demineralisation   demineralisation   fractionation   clarification
dewatering   dewatering   sugar removal
concentration   concentration   concentration
                                clarification

Figure 8.2. Summary of membrane liquid filtration processes.

8.2.1.1 Operational modes

Two distinct modes of filtration are relevant to membrane media, as shown schematically in Figure 8.3. *Dead-end* (or through-flow) *filtration* is the conventional mode for all filtration, with the feed flow perpendicular to the membrane surface; essentially all of the fluid passes through the membrane whilst the separated particles accumulate on its surface as a layer of retained solids. This build-up of solid particles leads to a progressive increase in the resistance to filtration through the membrane, to the point where flow eventually stops.

Table 8.1   Membrane separations and materials

Membrane separation	Membrane type	Driving force	Applications
Microfiltration	Symmetric and asymmetric microporous	Hydrostatic pressure	Clarification, sterile filtration
Ultrafiltration	Asymmetric microporous	Hydrostatic pressure	Separation of macro-molecular solutions
Nanofiltration	Asymmetric	Hydrostatic pressure	Separation of small organic compounds and selected salts from solutions
Reverse osmosis or hyperfiltration	Asymmetric, composite with homogenous skin	Hydrostatic pressure	Separation of micro-solutes and salts from solutions
Gas permeation	Asymmetric or composite, homogenous or porous polymer	Hydrostatic pressure concentration gradient	Separation of gas mixtures
Dialysis	Symmetric microporous	Concentration gradient	Separation of micro-solutes and salts from macromolecular solutions
Pervaporation	Asymmetric, composite non-porous	Concentration gradient. vapour pressure	Separation of mixtures of volatile liquids
Vapour permeation	Composite non-porous	Concentration gradient	Separation of volatile vapours from gases and vapours
Membrane distillation	Microporous	Temperature	Separation of water from non-volatile solutes
Electrodialysis	Ion exchange, homogeneous or microporous polymer	Electrical potential	Separation of ions from water and non-ionic solutes
Electrofiltration	Microporous charged membrane	Electrical potential	Dewatering of solutions of suspended solids
Liquid membranes	Microporous, liquid carrier	Concentration. reaction	Separation of ions and solutes from aqueous solutions

The formation of this surface filter cake can be reduced or eliminated by the use of tangential or *cross-flow filtration*. Only part of the fluid now passes through the membrane as filtrate (or, more correctly, permeate, since some membrane processes operate by permeation rather than filtration); the retained part, or retentate, consequently becomes more concentrated in particulate or solute species. The extent to which cross-flow successfully prevents the surface of the membrane being fouled by deposited particles is dependent on a variety of factors, especially the cross-flow velocity. Chemical and/or mechanical procedures are usually required to clean (and sterilize) the membrane, which must be able to withstand the associated mechanical, chemical and thermal stresses. Whereas microfiltration utilizes both the dead-end and cross-flow filtration, cross-flow is the usual mode for the other membrane filtration processes, and has grown to its present level of importance from its beginnings in reverse osmosis.

8.2.1.2 Operational problems

The build-up of a 'fouling' layer on the surface of a membrane is one of the most serious problems in membrane processes. The term 'fouling', rather than the more familiar 'filter cake', arose from the origins of membrane processes in molecular separations, where macromolecular proteins would separate on to the membrane surface as a slimy, gel layer, which rapidly reduced the fluid flux through the membrane. Fouling layers have to be removed periodically by cleaning, as mentioned above, but much ingenuity is employed by membrane system designers to minimize fouling layer formation.
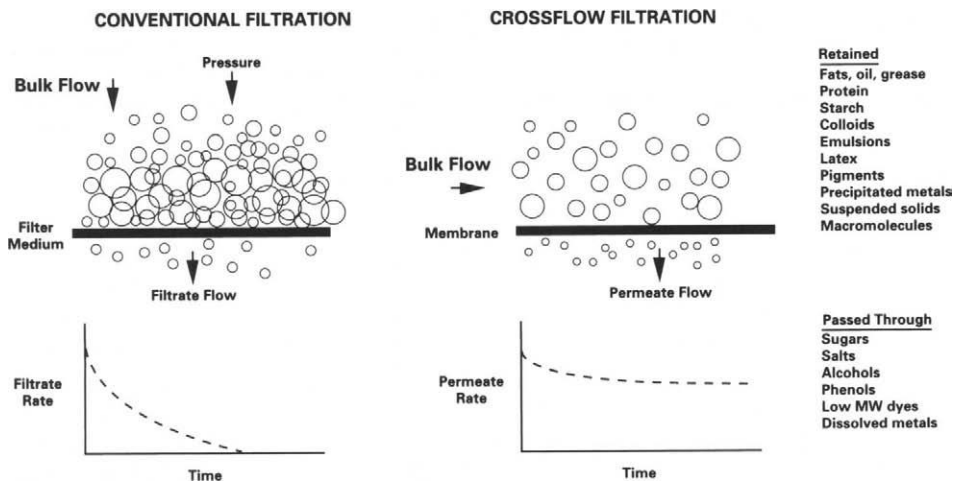

Figure 8.3. Comparing cross-flow filtration with conventional filtration.

Another operating problem, concentration polarization, affects the membrane processes dealing with suspended or dissolved species. The molecules to be separated (i.e. kept in the retentate) diffuse through the liquid close to the membrane surface and become much more concentrated at the surface, creating a different kind of barrier to liquid flow, and so reducing flux. In the same way, the particulate matter accumulates in the liquid as it approaches the boundary layer, creating a similar resistance to liquid flow.

There are basically three types of method employed to reduce fouling and/or concentration polarization, and so increase flux rates:

- changes in the surface characteristics of the membrane;
- conditioning of the feed slurry/solution; and
- modifications in the way the fluid/membrane is operated.

An example of the way in which the membrane material itself may be modified is given by Kalsep's Kalmem LF membrane[2]. This is basically a polyethersulphone (PES) material, with polymeric low-fouling additives incorporated into the PES. The chemically modified surface is permanently hydrophilic, and can be made with pore sizes in the microfiltration and ultrafiltration ranges.

The surface of the membrane needs to be as smooth as possible, and the slurry or solution as free as possible of material that will foul the surface. Operational modifications are generally designed to create some kind of shearing or scouring of the fouling layer. Some of these are mechanical, and are discussed in the next section, while the use of a two-phase (gas/liquid) flow[3] is growing in importance.

8.2.2 Membrane formats

Depending on the properties of the material used, membranes may be produced in the following geometrical forms:

- flat sheets – self-supporting or backed by a supporting substrate (and including the sheets when rolled up into a spiral-wound configuration);
- tubes – self-supporting or backed by a supporting substrate, typically 12–24 mm in internal diameter; and
- hollow fibres – typically 40 μm internal diameter × 80 μm outside diameter.

All of these forms are mostly utilized by being incorporated in filter cartridges, such as are described in Chapter 9. Some of the more robust types of membrane sheets can be used in industrial process filters such as filter presses. For laboratory duties, sheet membranes are available as discs in a range of standard diameters; appropriate grades are also supplied in roll form.

Because of the high fluid flow resistance of most membranes, they are usually operated in some kind of module, which allows the largest possible filtration area

to be packed into the smallest possible equipment volume. There are six distinct styles of module in which membrane media are employed: flat sheet, pleated sheet, spiral wound sheet, tubes or tube bundles, perforated blocks and hollow fibre bundles. Polymeric membranes are used in almost all forms – except the perforated block, which is very largely restricted to inorganic materials.

Flat sheet modules are based on the principle of the plate-and-frame filter press, comprising an alternating stack of sheets of membrane media and separator plates through which the feed, retentate and permeate flow. These are the least compact of the different module formats, and are correspondingly the least used. Figures 8.4 and 8.5 show, respectively, a laboratory and a free-standing industrial flat sheet module of this type, which can be used for microfiltration or ultrafiltration. Most polymeric materials, and much of the inorganic materials are available as flat sheets or rolls, and can be used in this type of module, which finds most application in laboratory and pilot plant. For example, Tami Industries KaCeram media are available for microfiltration in the range 0.14–1.4 μm, and for ultrafiltration in the range 15–300 kD.

If the flat sheet medium is sufficiently flexible, then it can be pleated, just as can any other paper-like material. In this way, a membrane can be used for absolute air filtration, as in Chapter 5, as a filter bag for gas cleaning or as a cartridge filter, as described in Chapter 9. Pleating is possible for most polymeric media, for some metallic media, and even for some ceramics.

Membrane materials can also be made or cut into long, wide strips, which are then rolled up around a central former, with appropriate sheets of spacers and
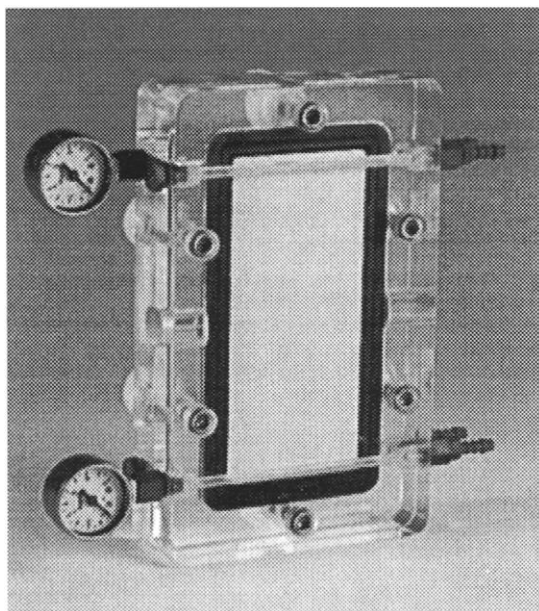

Figure 8.4. A laboratory scale 'Pleiade Rayflow 100' cross-flow filter with a membrane area of 100 cm². (Photograph: Ultra-Tech Services Ltd)

supports sandwiched between the membrane layers, to create a *spiral wound module*, as illustrated in Figure 8.6. Such a construction gives a very compact unit containing a large membrane area. For example, a module that is just 200 mm in diameter and 900 mm long may contain up to 23 m² of active membrane. Because the sandwich structure operates with very small clearances between the sheets, it is essential that adequate prefiltration is undertaken of the feed liquid. Spiral wound modules are used for microfiltration and ultrafiltration.

Simple tubes are feasible as membrane formats, but unlikely outside the laboratory, because of their small area. Much more likely, on the industrial scale, are *tubular modules*, with bundles of tubes constructed in the same form as a shell-and-tube heat exchanger, as shown in Figure 8.7. In the version illustrated, each replaceable 12.5 mm diameter membrane tube fits into a perforated stainless steel support tube. The membrane tubes, which can be several metres in length, are of composite construction, with, for example, a cellulose acetate membrane cast on to the internal surface of a synthetic fibre support tube.

An alternative approach is offered by the three options illustrated in Figure 8.8, all of these being disposable items. The single 25 mm i.d. tube version has an inside layer of PES membrane cast onto an epoxy resin reinforced fibreglass support, with an outside protective tube of PVC. The Ultra-cor VII tube is divided internally by a bundle of seven 12.5 mm membrane tubes, thereby increasing the available filtration are a per unit length; this concept is extended further in the Super-cor tube, with its array of 21 internal tubes.

The tubular formats are the ones most likely to be adopted for inorganic media, especially for ceramics, where the idea is further extended into the *perforated block* structure illustrated in Figure 8.9. A monolithic block, of very coarsely porous ceramic, shaped to fit into a containing tube, is perforated with a number of cylindrical channels parallel to its length. A ceramic membrane layer is then
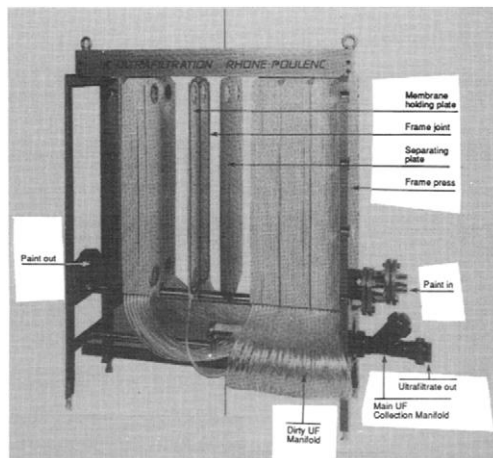

Figure 8.5. A 'Pleiade' UFP71 ultrafiltration filter, with a total membrane area up to 21 m² can be used on applications such as recovering paint from a car spraying unit.

laid down on the inner surface. A very wide range of channel number and shape is possible with this kind of construction – the range currently marketed by Tami Industries covers 14 different shapes, with up to 39 individual channels offering hydraulic diameters from 2 to 14 mm. These all have quite thin walls through which the permeate must pass.

Hollow fibre modules are also in the basic format of a shell-and-tube heat exchanger, but now the tubes are hollow fibres with outside diameters ranging from a few millimetres down to as fine as a human hair (about 80 μm). These fibres, which may be several hundreds in number, are assembled as a closely packed bundle, sealed at its ends into resin plugs, either at opposite ends of the containing shell, as in Figure 8.10, or with the bundle looped round and the ends sealed into the same plug, as in Figure 8.11. As indicated by these two figures,
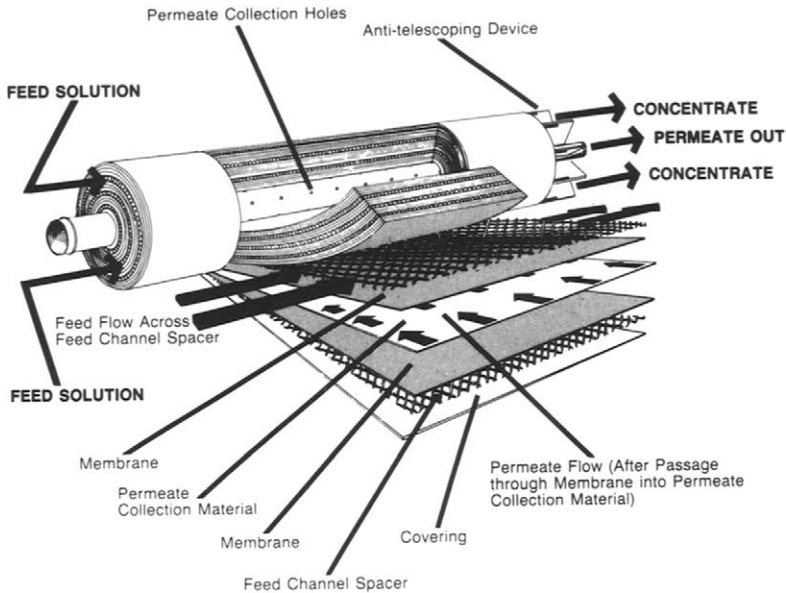

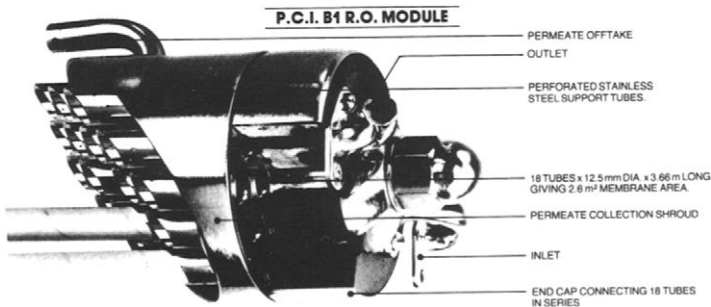*Figure 8.6. A spirally wound MF or UF module.*

Figure 8.7. Part of a PCI tubular RO module.

the fluid to permeate flow direction can be either in-to-out or out-to-in for hollow fibre applications.

A great advantage of the hollow fibre module is its compactness in relation to its very large filtration area per unit volume, typically $8000 \, m^2/m^3$. For example, with a Koch standard 1.09 m long, 0.127 m diameter module, the membrane area is $3.7 \, m^2$ with 2.7 mm diameter fibres, and $12.3 \, m^2$ with 0.5 mm fibres.

A general comparison of the main types of membrane module is provided in Table 8.2.

In all of the module designs discussed above the membrane medium is stationary, and the fluid flows across (or occasionally through) it. However, as stated earlier, the problems of fouling and concentration polarization can be at
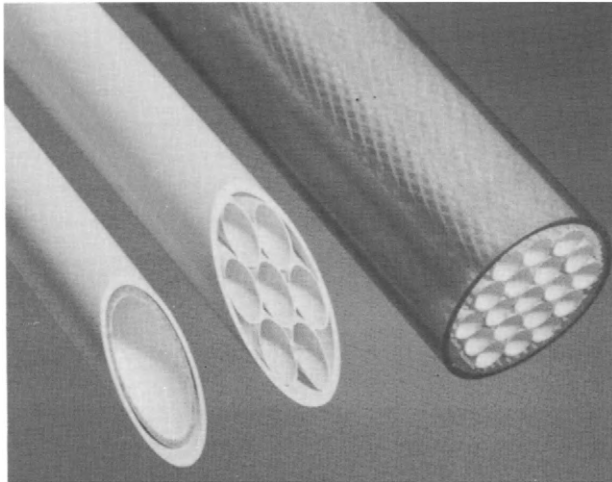

Figure 8.8. Tubular MF/UF/RO options: single tube, 'Ultra-cor VII' and 'Super-cor'.

Multiple layers of alumina are sintered to form a monolithic Membralox element which will not delaminate, swell, or compact—even under elevated temperature, high operating pressure, or reverse flow conditions.

Feed stream channels within the porous alumina structure are lined with a selective membrane layer. Pore diameters range from 0.2 to 5 μm pores for microfiltration and 50 to 1,000 Å pores for ultrafiltration.
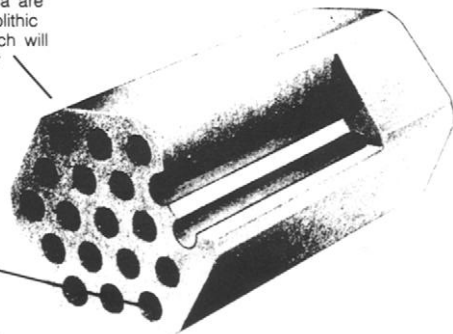

Figure 8.9. Sectional view of a 19-channel ceramic element. (Illustration: APV Membrantechnologie GmbH)

least partly reduced if an element of shear can be applied to the boundary layer at the membrane surface. This can be achieved either by causing the membrane to rotate or oscillate with relation to the fluid flow. Still very much in the development phase, the rotating moving membranes can be in the form of a disc[4] or a cylinder[5], while a stack of discs is caused to oscillate in another variant[6], which has reached commercial use. SpinTek Filtration Systems introduced a rotating ultrafiltration unit, using a ceramic membrane, into commercial use in mid-1999.

8.3 Membrane Materials

To be effective for separation, membranes should exhibit appropriate characteristics, such as good chemical resistance (to both feed and cleaning fluids), mechanical stability, thermal stability, high permeability, high selectivity and general stability in operation; for guidance on the chemical compatibility of membrane materials, see Table 8.3 (originating with Millipore Inc), or the more detailed Table 2.4 for fabrics in Chapter 2.
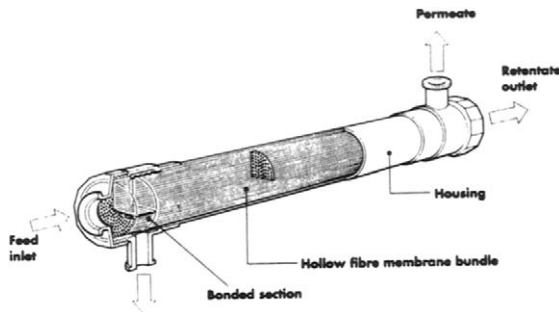

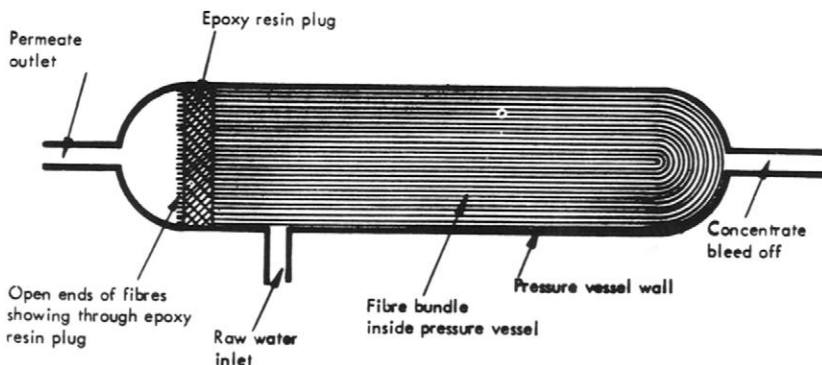*Figure 8.10. A hollow tube module with in-to-out flow.*

Figure 8.11. A hollow tube RO module with out-to-in flow.

Table 8.2   General comparison of characteristics of membranes

Tubular membranes
1. Tubular modules have relatively large channel diameters, and are capable of handling feed streams and slurries containing fairly large particles. The general rule of thumb is that the largest particle that can be processed in a membrane module should be less than one-tenth the channel height. Thus feed streams containing particles as large as 125 μm can be processed in 1.25 mm tubular units.
2. Tubular units of 1.25–2.5 cm diameters are operated under turbulent flow conditions with recommended velocities of 2–6 m per second. Flow rates are 15–60 l per minute per tube, depending on the tube diameter. Reynolds numbers are usually greater than 10 000.
3. Pressure drop averages 2–3 psi per 2.4–3.6 m tube. Thus, typical pressure drops for 12–25 mm tubes will be approximately 30–40 psig (2–2.5 bar) for UF units operating in parallel flow under these flow conditions. This combination of pressure drop and high flow rates gives high energy consumption.
4. The open tube design and the high Reynolds numbers make it easy to clean by standard clean-in-place techniques. It is also possible to insert scouring balls or rods to help clean the membrane.
5. Tubular units have the lowest surface area to volume ratio of all module configurations.
6. In certain modules the individual membranes can be replaced fairly easily in plant resulting in considerable savings in transportation costs and membrane costs.
7 Tubular module costs vary widely from about $100 to 800/m^2 for replacement membranes of cellulose acetate, polysulphone or composites.

Hollow fibre modules
1. The recommended operating velocity in the UF hollow fibre system is around 0.5–2.5 m/s. This results in Reynolds numbers of 500–3000. Hollow fibres thus operate in the laminar flow region.
2. Shear rates are relatively high in hollow fibres due to the combination of thin channels and high velocity. Shear rates at the wall are 4000–14 000/s.
3. Hollow fibres have the highest surface area-to-volume ratio. Hold-up volume is low, typically 0.5 l in a typical 'short' cartridge of 1.4–1.7 m^2 membrane area.
4. Pressure drops are typically 0.3–1.3 bar depending on the flow rate. The combination of modest pressure drop and flow rates make hollow fibre modules very economic in energy consumption.
5. Hollow fibres have only a modest maximum pressure rating of about 1.8 bar. The short (30 cm) cartridge can withstand pressures up to about 2.4 bar at low temperatures (less than 30°C). Several process streams are dilute enough to permit UF operation at pressures much higher than the present 1.7 bar limiting transmembrane pressure. In addition, since the flow rate is proportional to pressure drop, flow rates are limited since the inlet pressure cannot exceed 1.7 bar. This can be problematic with highly viscous solutions, especially with long cartridges.
6. The small fibre diameters make them susceptible to plugging at the cartridge inlet. To prevent this the feed should be prefiltered to at least 10 μm.
7. Hollow fibres are suitable for 'back-flushing' because the fibres are self-supporting. This vastly improves performance due to cleaning *in situ* potential.
8. Replacement membrane costs are relatively high. Damage to one single fibre out of the 50–3000 in a bundle generally means the entire cartridge has to be replaced. However, it is possible to repair membrane fibres *in situ* in certain cases.
9. The cost is about $700 per 7.5 cm industrial cartridge, regardless of surface area. Replacement cost is about $230–350/m^2.

Plate
1. The typical plate channel height is between 0.5 and 1.0 mm. UF systems operate under laminar-flow, high shear conditions. The channel length (the distance between the inlet and outlet ports) is between 6 and 60 cm. The Grober equation agrees reasonably well with experiment in the Reynolds number range of 100–3000 for slits of channel height 0.4–1.0 mm.

Table 8.2 (*continued*)

2.   The permeate from each pair of membranes can be visually observed in the plastic tubing coming from each support plate. This is convenient for several reasons, e.g. detection of leaks in a particular membrane pair, if samples need to be taken for analysis, or if flux measurement as a function of capacity needs to be made.

3.   Replacement of membranes on site is relatively easy provided that care is taken when closing the stack of plates together. The previously embedded grooves of the unreplaced plates must match exactly as they were previously, or else leakage of feed can occur.

4.   In horizontal modules, the flow is parallel through all channels at velocities of about 2 m/s. For a stack of plates, this can result in a pressure drop of about 10 bar. Plate-and-frame systems tend to be intermediate between spiral-wound and tubular systems in energy consumption for recirculation.

5.   Membranes are currently about $120/m^2$ for cellulose acetate, $230/m^2$ for non-cellulosic RO membranes, and $140/m^2$ for polysulphone membranes.

6.   Surface area-to-volume ratio is fairly high, averaging about $600-1000 \, m^2/m^3$.

Spiral wound

1.   In spiral-wound modules the feed channel height is controlled essentially by the thickness of the mesh-like spacer in the feed channel. Spacers of 0.76 or 1.1 mm are most common. The advantage of a narrow channel height is that much more membrane area can be packed into a given pressure vessel.

2.   A larger channel height, while reducing the surface area-to-volume ration slightly, may be more desirable to minimize pressure drops and reduce feed channel plugging. The general rule of prefiltering to one-tenth the channel height is modified for the spiral-wound unit due to the presence of the spacer which reduces the free volume in the channel. Prefiltration of the feed down to $5-25 \, \mu m$ is recommended for the 0.76 mm spacer-module, and $25-50 \, \mu m$ for the 1.1 mm channel.

3.   Lengths of individual membrane assemblies vary from 1 to 6 feet (0.3–2 m). When calculating the surface area of a spiral-wound membrane, it is convenient to consider it as two flat-sheets, although the *effective* membrane area of spiral-wound modules must allow for gluing the membrane sandwich, for fixing the fourth side to the permeate collection tube and the outer periphery.

4.   The hydrodynamics in the spiral-wound module is not too clear. The velocity in spiral-wound units ranges from 10 to 60 cm/s, being higher for the large mesh spacers. These are 'superficial' velocities, however, since the volume occupied by the mesh-like spacer in the feed channel is neglected. These velocities correspond to Reynolds numbers of 100–1300. Technically, this is in the laminar flow region, but the additional turbulence contributed by the spacers means that the flow is in the turbulent region.

5.   Surface area-to-volume ratio is fairly high, averaging about $600-1000 \, m^2/m^3$.

6.   Pressure drops in the feed channel are relatively high due to the effect of the spacer. At a superficial velocity of 25 cm/s the pressure drop is around 1–1.4 bar. This high pressure drop can give rise to a 'telescoping' effect at high flow rates, i.e. the spiral pushes itself out in the direction of flow. This can damage the membrane and so anti-telescoping devices are used at the downstream end of the membrane element to prevent this.

7.   The combination of the low flow rates, pressure drops and relatively high turbulence makes this an economic module in terms of power consumption. A problem with the mesh spacers is the creation of 'dead' spots directly behind the mesh in the flow path. This may cause particles to 'hang up' in the mesh network, resulting in cleaning problems. This makes it difficult to process feeds containing suspended particles, especially if it is a concentrated slurry and a high recovery of the particles is required. Spiral modules work best on relatively clean feed streams with a minimum of suspended matter.

8.   Capital costs are quite low. The membrane element can be recovered from the pressure vessel and returned to the factory for reassembling new membranes. Replacement membranes are priced typically at $35-140/m^2$ for cellulose acetate, polyvinylidenedifluoride, and polysulphone membranes.

Table 8.3   Chemical compatibility of membrane materials

	Cellulose acetate	Hydrophobic PVDF	Hydrophilic PVDF	MF-Millipore cellulose esters	Fluoropore PTFE	Mitex PTFE	Isopore PC polycarbonate	Isopore PET polycarbonate	AN and PP polypropylene
Acids									
Acetic acid, glacial	X	●	●	X	●	●	O	●	●
Acetic acid, 5%	●	●	●	●	●	●	●	●	●
Boric acid	●	●	●	●	●	●	●	–	●
Hydrochloric acid (conc.)	X	●	●	X	●	●	●	X	●
Hydrofluoric acid	X	●	●	X	●	●	●	X	O
Nitric acid (conc.)	X	O	X	X	O	●	●	X	O
Sulphuric acid (conc.)	X	●	X	X	O	●	X	X	●
Bases									
Ammonium hydroxide (6N)	X	●	X	X	●	●	X	O	●
Sodium hydroxide (conc.)	X	●	X	X	●	●	X	X	●
Solvents									
Acetone	X	X	X	X	●	●	O	●	●
Acetonitrile	X	●	O	X	●	●	–	–	O
Amyl acetate	X	●	●	X	●	●	●	●	X
Amyl alcohol	X	●	●	X	●	●	●	●	●
Benzene	X	●	●	●	O	●	O	●	O
Benzyl alcohol (1%)	O	●	●	●	●	●	●	●	●
Brine (sea water)	●	●	●	●	●	●	●	●	●
Butyl alcohol	●	●	●	●	●	●	●	●	O
Carbon tetrachloride	X	●	●	●	O	●	O	●	X
Cellosolve (ethyl)	X	●	●	X	●	●	–	●	O
Chloroform	X	●	●	●	O	●	X	●	O
Cyclohexanone	X	●	●	X	●	●	●	●	X
Dimethylacetamide	X	X	X	X	●	●	–	–	O
Dimethylformamide	X	X	X	X	●	●	X	●	●
Dioxane	X	●	●	X	●	●	X	●	O
DMSO	X	●	●	X	●	●	X	●	●
Ethyl alcohol	●	●	●	O	●	●	●	●	●
Ethers	O	●	●	●	●	●	●	●	X
Ethyl acetate	X	●	●	X	●	●	O	●	●
Ethylene glycol	●	●	●	X	●	●	●	●	●
Formaldehyde	●	●	●	X	●	●	●	●	●
Freon TF or PCA	X	●	●	●	●	●	●	●	X
Gasoline	X	●	●	●	●	●	●	●	●
Glycerine (glycerol)	●	●	●	●	●	●	●	●	●
Hexane	X	●	●	●	●	●	●	●	●
Hydrogen peroxide (3%)	X	●	●	X	●	●	●	●	●
Hypo (photo)	–	●	●	●	●	●	–	●	●
Isobutyl alcohol	●	●	●	●	●	●	●	●	●
Isopropyl acetate	O	●	●	X	●	●	–	●	●
Isopropyl alcohol	●	●	●	X	●	●	●	●	●
Kerosene	X	●	●	●	●	●	●	●	

Table 8.3 (*continued*)

	Cellulose acetate	Hydrophobic PVDF	Hydrophilic PVDF	MF-Millipore cellulose esters	Fluoropore PTFE	Mitex PTFE	Isopore PC polycarbonate	Isopore PET polycarbonate	AN and PP polypropylene
Methyl alcohol	●	●	●	X	●	●	●	●	●
Methylene chloride	X	X	●	X	O	●	X	●	X
MEK	X	X	X	X	●	●	O	●	●
MIBK	X	●	X	X	●	●	–	–	●
Mineral spirits	X	●	●	●	●	●	●	●	●
Nitrobenzene	X	●	●	X	●	●	X	●	●
Paraldehyde	X	●	●	X	●	●	–	–	–
Ozone (10 ppm in water)	X	●	●	●	●	●	●	–	●
Pet base oils	X	●	●	●	●	●	●	–	–
Pentane	X	●	●	●	●	●	●	●	X
Perchloroethylene	X	●	●	●	O	●	●	●	X
Petroleum ether	X	●	●	●	●	●	●	●	X
Phenol (5.0%)	X	●	●	●	●	●	–	●	●
Pyridine	X	●	●	X	●	●	X	●	●
Silicon oils	X	●	●	●	●	●	●	●	●
Toluene	X	●	●	●	O	●	O	●	O
Trichloroethane	X	●	●	●	O	●	O	●	X
Trichloroethylene	X	●	●	●	O	●	X	●	X
TFA	X	●	O	X	●	●	–	–	●
THF	X	●	●	X	●	●	X	●	O
Xylene	X	●	●	●	O	●	●	●	O
Gases									
Helium	X	●	●	●	●	●	●	●	●
Hydrogen	X	●	●	●	●	●	●	●	●
Nitrogen	X	●	●	●	●	●	●	●	●
Ozone	X	X	X	X	X	●	●	O	O

Codes: ● = recommended; O = limited applications. testing prior to use is recommended;
X = not recommended.

Recommendations are based upon static soak for 72 h at 25 C and atmospheric pressure. Dynamic (operating) conditions at moderate (±10%) fluctuation will not change the recommendations, but high liquid temperature may do so in some cases.

8.3.1 Range of membrane materials

Originally, all membranes were based on natural materials or derivatives of natural cellulose. Whilst cellulosic media continue to play an important role in certain areas of application, the major source of membranes is now synthetic polymers, some of which are included in Table 8.4. There is an immense variety of polymeric materials available as filter media, including grades with specially

Table 8.4   Typical characteristics and applications of microfiltration membranes

Material	Characteristics	Typical applications
Polysulphone	An inherently hydrophilic polysulphone membrane with excellent flow rates, low extractables, broad chemical compatibility, high mechanical strength and temperature resistance.	Food and beverages Pharmaceuticals Semiconductor water Serum
Nylon	Hydrophilic membrane with high tensile strength. Very high flow rates, long life and low extractables. Offers excellent chemical compatibility.	Semiconductor water Chemicals Beverages
PTFE	Naturally hydrophobic membrane laminated to a polypropylene support for extra durability and strength. Superior chemical and temperature resistance.	Air and gases Pharmaceuticals Aggressive chemicals
Acrylic copolymer	Inherently hydrophilic copolymer with strong nonwoven polyester fabric support. Offers high flow rates, low differential pressures and low extractables.	Semiconductor water Pharmaceuticals Food and beverages
Polypropylene	Naturally hydrophobic membrane and chemically inert. Broad pH stability, high temperature resistance and high flow rates.	Chemicals Microelectronics Pharmaceuticals
Glass	Nominal 1.0 mm fine borosilicate glass fibre. High flow rates at moderate differential pressures. Good wet strength and high dirt-holding capacity.	Chemicals Serum Beverages
Polycarbonate	Hydrophilic membrane, unique pore structure and capture, strong, flexible, high flow rate, thermal stability, non-extractable.	Pharmaceuticals Air pollution Laboratory analysis
Cellulose	Hydrophilic membrane. General purpose, with limited thermal and mechanical stability. Some extractables.	Air pollution Microbiology Foods and pharmaceutical

developed properties: hydrophobic or hydrophilic, anionic or cationic, for specific filtration applications.

The range of synthetic polymers used for membrane media includes:

- acrylics
    polyacrylonitrile (PAN)
    acrylic copolymers
- amides and imides
    nylons and aliphatic polyamides
    polyaramids (aromatic amides)
    polyimide and polyetherimide (PEI)

- esters
    polycarbonate (PC)
    polyethylene terephthalate (PET) and polybutylene terephthalate (PBT)
- fluoropolymers
    polyvinylidenedifluoride (PVDF)
    polytetrafluoroethylene (mostly as ePTFE)
- ketones and sulphones
    polyetherketone (PEK) and polyetheretherketone (PEEK)
    polysulphone, polyethersulphone (PES)
- olefins
    polyethylene (usually high density) (HDPE)
    polypropylene (PP).

Of these, PC, ePTFE and PES are among the fastest growing in importance. Most of these types of membrane material are reviewed in the next section.

During the last 20 years or so, inorganic materials such as ceramics and metals have become of increasing significance as membrane materials. The introduction of these, despite their being nearly an order of magnitude more expensive than their organic counterparts, has occurred because of their much-improved operating lifetimes, their robustness, their greater tolerance to extreme conditions of operation, such as higher temperature and aggressive chemicals, and the subsequent overall saving in lifetime costs.

Apart from the doped PES referred to above, in Section 8.2.1, for anti-fouling performance, most membranes have a single polymer (or copolymer) as the active layer. A quite different kind of membrane, the *affinity membrane*, is developing rapidly as a separation tool[7], able to separate molecular species by their chemical characteristics, rather than by size. These are based on the molecular recognition technology that won the 1987 Nobel Prize for Chemistry, and are marketed by 3M.

8.3.2 Membrane properties

The irregularity of the pores of most membranes, and the often irregular shape of the particles being filtered, results in there not being a sharp cut-off size during filtration. With symmetric membranes some degree of depth filtration could occur as smaller particles move through the tortuous flow path. To counteract this effect, asymmetric membranes, which have surface pore sizes much less than those in the bulk of the membrane material, are used to trap the particles almost exclusively at one surface (the membrane skin) whilst still offering low hydrodynamic resistance.

A membrane that is *hydrophobic* will have a greater tendency to being fouled, especially by proteins. Hydrophobic membranes require wetting, for example with alcohol, prior to filtration of water-based solutions: they are consequently good filtration media for gases. Three hydrophobic materials commonly used as microfiltration membranes are PTFE, PVDF (polyvinylidenedifluoride) and

polypropylene. These all exhibit excellent to good chemical stability. PTFE is insoluble in most common solvents and is produced by solvent casting. PVDF is less stable than PTFE, and is soluble in aprotic solvents such as dimethylformamide, and can be produced by solvent casting. Polypropylene is the least stable of the three and can be produced by stretching and phase inversion.

Many polymer membrane materials exhibit detrimental adsorption characteristics. Solute adsorption has the effect of reducing flux, and can lead to difficulties in membrane cleaning. *Hydrophilic* membranes are consequently widely used because of their reduced adsorption behaviour. The best-known hydrophilic materials are based on cellulose, such as cellulose ester (acetate, triacetate, nitrate and mixed esters). Cellulose is a polysaccharide, derived from plants, and is quite crystalline; the polymer is very hydrophilic but is not water soluble. Cellulose acetate is a relatively inexpensive hydrophilic material that has good resistance to fouling in many applications, especially with proteins; however, it has a limited pH operating range (3–7), and its operating temperatures need to be below 35°C, while the polymer is very susceptible to biological degradation. Other hydrophilic membranes commonly used are polycarbonate, polysulphone, polyethersulphone and nylon. More recently, ceramic membranes (mainly alumina and zirconia) have become routinely used in more demanding applications. Membranes made from glass, carbon and metals (including silver, aluminium and stainless steel) are used for special applications.

Polysulphone is an engineering polymer used for both microfiltration and ultrafiltration membranes. The ultrafiltration versions are available with a nominal molecular weight cut-off (MWCO) in the range 2–100 kD. Polysulphone exhibits quite good chemical and temperature stability (up to 80°C) and can function in the pH range 1.5–12 for short periods of cleaning. It exhibits some resistance to oxidizing agents (e.g. chlorine) but on prolonged exposure to such materials it will lose its separation characteristics.

PVDF has similar, if not better, pH and temperature tolerances than polysulphone and has a superior tolerance to oxidizing agents and many solvents. It thus can be cleaned with more aggressive agents for substantially longer periods. It is available as an anisotropic membrane, produced by phase inversion.

Polyacrylonitrile is used either alone or as a copolymer, with for example PVC or methyl methacrylate added to increase its hydrophilicity, for ultrafiltration. It offers a tolerance to a wide range of organic solvents.

Semi-crystalline aromatic polyetherketones form an extremely useful range of high-performance engineering polymers, with a unique combination of mechanical toughness, high modulus, hydrolytic stability, resistance to oxidative degradation, the retention of physical properties at moderately high temperatures (up to 250°C), and the ability to withstand organic solvents such as toluene and tetrachloroethylene; these materials are steam sterilizable.

Polyamides are another important class of membranes with good chemical, thermal and mechanical stability. Aliphatic polyamides, such as Nylon-6, Nylon 6-6 and Nylon 4-6, are used as microfiltration and ultrafiltration membranes.

8.4 Membrane Manufacture

Factors that have a profound influence on the structure or morphology of a particular membrane are the nature of the process by which it is manufactured and the form of the raw material used. The various manufacturing processes, which are discussed in this section, can be broadly summarized as:

- sintering of fine graded particles;
- solvent casting or phase inversion, involving the stage-wise evaporation of a solution of polymer in a mixture of solvents;
- irradiation and etching of an impervious film; and
- stretching an impervious film to cause multiple ruptures.

Figures 8.12 and 8.13 respectively provide schematic and photographic representations of the resultant variety of morphologies – strictly speaking for microfiltration membranes only, but actually applying to all kinds.

he manufacturing processes for membranes are actually quite numerous, as shown in Table 8.5. In presenting a brief description of these processes, it is appropriate to distinguish between polymeric membranes, which formerly dominated the whole field, and the increasingly important membranes based on inorganic materials.

8.4.1 Manufacture of polymeric membranes

Polymeric membranes for microfiltration are manufactured by several processes, including stretching, phase inversion (solvent casting) and track etching, as well as sintering. In the case of ultrafiltration membranes, the usual method of preparation is phase inversion, as it is for reverse osmosis and nanofiltration media; ultrafiltration membranes are sometimes used as supports for the production of composite membranes for reverse osmosis and gas permeation.

8.4.1.1 Sintering

The production of membranes by sintering involves the compressing of a powder of particles of carefully graded size, and then heating to an elevated temperature. With the correct temperature of sintering for the specific material, the interface between the particles disappears to produce a porous structure. The pore size produced depends on the particle size and size distribution, but is limited to sizes of 0.1 μm or more. Porosity of the membrane is relatively low, typically in the range 10–20% for polymers (but up to 80% for metal membranes). The method is also used to produce membranes of ceramic, carbon and glass.

8.4.1.2 Stretching

The patented stretching process invented by W L Gore Inc converts impervious PTFE film into a range of membranes. The essence of the process is to subject the hot film to an extremely rapid unidirectional stretching action at about 320°C,

SYMMETRIC MICROFILTRATION MEMBRANES

| pore structure	straight pores	soap bubble-like (foam-like)	coral-like (tortuous)	stretched
production technique	track-etching/ anodising processes	casting + leaching/evaporation		film-stretching

ASYMMETRIC MICROFILTRATION MEMBRANES

| pore str.	finger-like substructure sieve-like toplayer	foam-like substr. nodular toplayer	double toplayer	sintered ceramic spheres
production technique	phase inversion	phase inversion	phase inversion	sintering/ slip casting

Figure 8.12. Morphologies of microfiltration membranes.
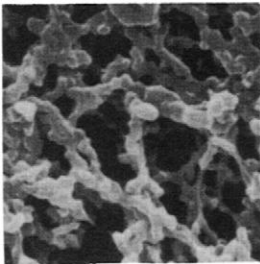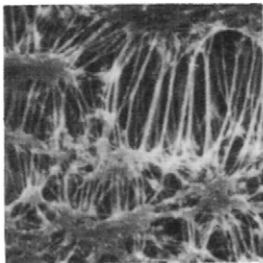

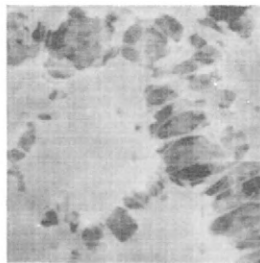
Mixed esters of cellulose membrane.
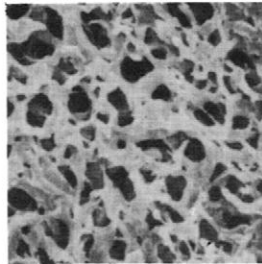
Durapore polyvinylidene difluoride membrane.
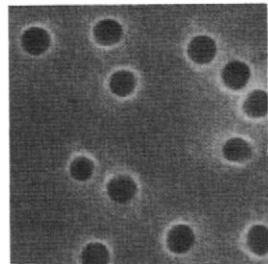
Isopore track-etched polycarbonate membrane.

Fluoropore PTFE membrane.

Solvex polypropylene membrane.

Figure 8.13. Electromicrographs of the surfaces of MF membranes. (Photographs: Millipore Corporation)

Table 8.5   Summary of membrane materials and manufacturing processes

Nominal pore size (µm)	Membrane/ support	Manufacturing process	Module configuration	Mechanical, thermal and chemical stability	Degree of asymmetry
0.1–5	Polysulphone	Immersion precipitation	Hollow fibre	+	++
0.1–0.65	Polypropylene	Thermal precipitation	Hollow fibre/ tubular	++	−
0.1–0.4	Nylon-6		Hollow fibre/ tubular	++	−
0.1	Polysulphone Cellulose acetate Fluoropolymer	Several phase inversion techniques	Hollow fibre/ flat sheet	+	+
			Flat sheet	−	±
			Flat sheet	++	±
2–5	Polyethylene	Phase inversion technique	Tubular	+	−
0.02–0.4	Polypropylene	Stretching	Hollow fibre	++	−
0.1–5	Polysulphone	Immersion precipitation	Flat sheet	+	++
0.1–5	Fluoropolymer		Flat sheet	++	++
0.2–10	Nylon	Evaporation precipitation	Flat sheet cartridge	++	−
0.1–5	Polysulphone	Immersion precipitation	Spiral wound/ tubular	+	+
0.01–0.5	Polyvinylalcohol	Immersion precipitation	Hollow fibre	−	
0.2	Polysulphone/ Fluoropolymer	Phase inversion technique	Flat sheet (rotary module)		
0.2	Polyolefine	Phase inversion technique	Hollow fibre	++	
0.1–0.65	Cellulose nitrate Fluoropolymer	Evaporation/ immersion	Flat sheet	−	±
		Precipitation	Flat sheet	++	±
0.1–1.2	Polysulphone	Immersion precipitation	Spiral wound	+	
	Fluoropolymer		Spiral wound	++	
0.1–1.5	Fluoropolymer	Immersion precipitation	Flat sheet	++	+
0.2–5	Fluoropolymer	Evaporation/ immersion	Flat sheet	++	±
0.6–0.8	Nylon	Precipitation	Flat sheet	++	±
0.05–1	Poly(ether)imide	Immersion precipitation	Hollow fibre/ flat sheet	+	+
0.05–1	Polysulphone		Hollow fibre/ flat sheet	+	+
0.2	Polycarbonate	Track etching	Flat sheet		
0.025–0.2	γ-Al$_2$O$_3$	Anodic oxidation	Flat structure	±	−
0.2–5	α-Al$_2$O$_3$	Sintering/slip casting	Tubular	+++	++
0.1	ZrO$_2$/α-Al$_2$O$_3$		Tubular	+++	

Table 8.5 (*continued*)

Nominal pore size (μm)	Membrane/ support	Manufacturing process	Module configuration	Mechanical, thermal and chemical stability	Degree of asymmetry
0.2–3	Glass	Leaching of soluble phase	Tubular		
0.1	ZrO_2/C	Dynamically formed from suspension	Tubular	+	++
0.15–8	SiC	Sintering/slip casting	Tubular	+++	++
0.2–1	Carbon	–	Tubular	+++	++
0.2–1	α-Al_2O_3	Sintering/slip casting	Tubular	+++	++
0.2	SiC	Sintering/slip casting	Tubular	+++	++
0.6–0.14	ZrO_3/C	Dynamically formed from suspension	Tubular	++	++
0.05–0.3	Glass	Leaching of soluble phase	Hollow fibre	±	–

followed by a period of heat treatment at a somewhat higher temperature. The first stage generates a structure of small nodes (from less than 1 μm up to 400 μm) connected by a mass of fine fibrils, as shown schematically in Figure 8.14. The heat treatment step results in a change in the crystalline structure, giving what is termed 'amorphous locking', with a major increase in mechanical strength. A highly magnified view of a sample of this type of membrane is shown in Figure 8.15.

Whilst the process as summarized permits the direct manufacture of a range of membranes, all of high porosity and strength, their extreme thinness (12–75 μm) presents considerable handling problems. It is essential to combine them with a suitable substrate, so as to give a product that is handleable and robust enough to use. Depending on the intended application, substrates range from lightweight spunbonded polypropylene or polyester, to substantial fabrics, such as thick needlefelts. Figure 8.16 shows a Goretex membrane coating a 500 g/m² needlefelt, at the still higher magnification of ×900. The delicate structure of the membrane is clearly visible, as are the spherical particles of fly ash, their sizes ranging from 3 to 15 μm, trapped on the surface.

8.4.1.3 Track-etching

Track-etched membranes are the closest membrane analogues to a sieve, the membranes being essentially dense polymer films punctuated by cylindrical holes. Figure 8.17 shows the surface of a track-etched membrane, in which the holes are about 0.2 mm in diameter. These membranes are manufactured by a process divided into two steps: tracking and etching. During the tracking phase, a thin polymer film is unrolled at high speed while exposed to a fast-moving beam

of accelerated argon ions. The highly energetic ions pierce the polymer film and break the polymer chains, leaving 'tracks' that are then etched in baths of aggressive chemical agents (such as caustic soda) to convert them into clean, cylindrical pores of a defined uniform character.

The pore density of the membrane is controlled during the tracking step, by modifying the speed of the film, while the pore diameter is controlled during the etching step, by varying the immersion time in the etchant bath. The use of a highly energetic argon ion beam during the tracking step allows the piercing of thicker films than was possible in older processes. The beam of argon ions, accelerated in a cyclotron during the manufacturing, avoids radioactive
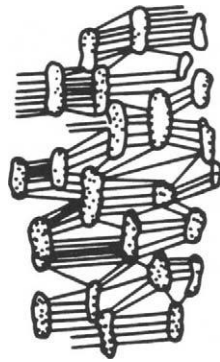

Figure 8.14. Schematic representation of the structure of Goretex membrane (from US Patent 3,953,566)
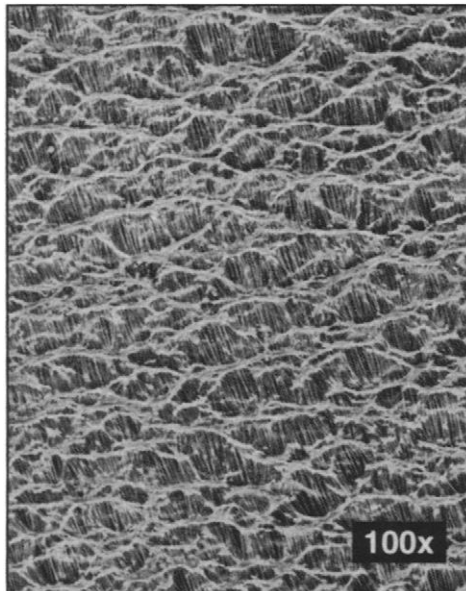

Figure 8.15. A microphotograph of expanded PTFE membrane. (Photograph: Tetratec Corporation)

contamination, and enables the etching to be performed immediately after the tracking step, reducing manufacturing time and improving quality control of the final product.

It has only proved possible to manufacture track-etched membranes with pore sizes in the microfiltration range (0.03–8 μm). Because these membranes are symmetric, their resistance to the flow of water is proportional to the membrane thickness, and they are therefore made thinner than asymmetric microporous membranes, in order to have comparable fluxes. The usual material that is track
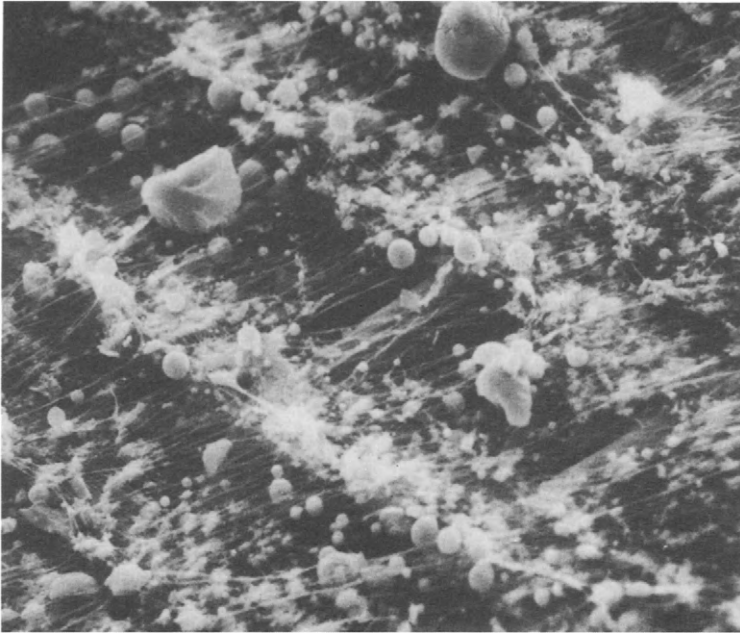
Figure 8.16. Fly ash particles on the Gore-Tex laminated surface of needlefelt.
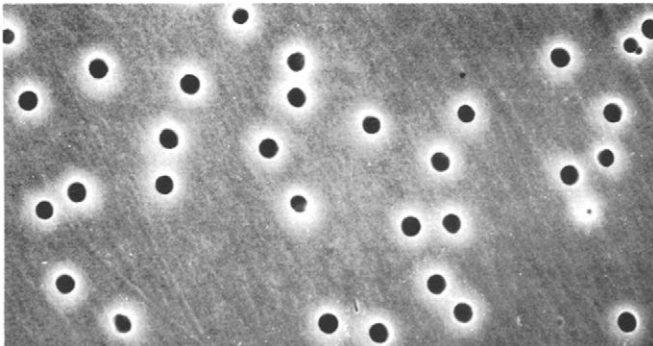
Figure 8.17. Surface of track-etched membrane showing regular hole size and distribution.

etched is polycarbonate, resultant porosities being of the order of 10%, depending on the radiation time.

8.4.1.4 Solvent casting or phase inversion

The majority of polymeric membranes can be produced by a method known variously as solvent casting or phase inversion, whereby a polymer solution inverts into a swollen three-dimensional macromolecular complex or gel. Porous membranes are produced from a two- or three- (or even four-) component dope mixture containing polymer, solvent and non-solvent (and salt in some cases).

The first step is to prepare a casting solution by dissolving polymer in a solvent, which may contain certain additives. To form flat membrane sheets, the casting solution is spread directly onto a suitable support by using a casting knife. The support may be a glass plate or other inert support, from which the membrane is then removed, or a support for the membrane itself (such as a non-woven polyester) to which the membrane remains fixed.

The casting thickness can typically vary from 50 to 500 μm. The cast film is then transferred to a non-solvent (gelation) bath, where exchange occurs between solvent and non-solvent (typically water), which leads to precipitation of the polymer from the solvent.

A typical example of the phase inversion manufacturing process, for cellulose acetate ultrafiltration membranes, is by dissolving the polymer in a mixture of acetone, dioxan and formamide. After precipitation has occurred, a thin skin of polymer forms on the surface of the cast film. The microstructure of the bulk of the membrane is determined in the gelation stage, although the process of gelation is strongly influenced by the properties of the skin at the surface of the membrane exposed to the air.

The invention of this basic process is attributed to Loeb and Sourirajan, an interesting account of whose pioneering work was provided in the opening paper[8] presented by Loeb to a four-day symposium of the American Chemical Society in 1980. This event was held specifically to mark the 20th anniversary of their development of the first modified asymmetric membranes with commercial potential for reverse osmosis.

Three types of membrane are typically produced in this way:

1. if the skin layer is dense, and has a very high resistance to the gelation medium and the outward transfer of the solvents, the rate of polymer precipitation can be limited by the rate of transfer across the skin, and a uniform porous structure is produced;

2. if the resistance of the skin is such that the rate of diffusion across the bulk of the membrane is more important, a gradation in pore size away from the skin surface is likely to occur, giving an asymmetric sponge-like structure;

3. membranes with finger-like voids are formed if the precipitation of polymer occurs rapidly, i.e. where solvents with little affinity for the polymer are used or where the gelation bath has a high salinity.

The performance characteristics (chiefly flux and selectivity) of phase inversion membranes depend upon many parameters, including polymer concentration, evaporation time before immersion, humidity, temperature,

composition of casting solution, and the composition and condition of the coagulation bath.

Hollow fibre membranes are produced by a different procedure, using various spinning processes (wet spinning, dry–wet spinning, melt spinning and dry spinning). The casting solution is pumped through a spinneret, which is a nozzle with a solid inner annular section that enables the solution to be extruded in a cylindrical form; this spinneret is used for the wet and wet–dry spinning processes. The hollow fibres are self-supporting and demixing occurs both outside and inside the fibre; after spending some time in the air, or in a controlled atmosphere, the fibre is then immersed in a non-solvent coagulation bath.

Tubular polymer membranes require a different procedure since they are not self-supporting. The casting has to be carried out on a supporting tubular material, such as non-woven polyester or carbon.

A variety of other methods for forming membranes by phase inversion are summarized in Table 8.6. Certain polymer membranes cannot be produced by conventional solvent casting because their crystallinity makes them insoluble in conventional solvents at ambient temperatures. This problem can be overcome by thermal phase inversion, in which a polymer is dissolved in a solvent at a high temperature, the solution then being cooled to precipitate the polymer as a formed membrane from which the solvent is removed. Polymeric materials made into membranes in this way include polyethylene, polypropylene, polycarbonate and PVC.

An alternative thermal phase inversion process permits the production of ultrafiltration and microfiltration membranes from aromatic polymers containing in-chain ether or thioether and ketone linkages. Suitable materials are homopolymers such as polyetherketone (PEK) and polyetheretherketone (PEEK), or copolymers such as PEK/PEEK and PEEK/PES (polyethersulphone). The first step is to dissolve the polymer in a 'latent' solvent, which is a compound

Table 8.6   Phase inversion membrane preparation

Precipitation method	Principle
Solvent evaporation	Evaporation on inert support or porous substrate in an inert atmosphere. Produces dense membranes (homogenous).
Vapour phase	Casting of film into a vapour phase of solvent and non-solvent. Membrane formation is due to penetration of non-solvent into cast film, producing a porous membrane with no top layer.
Controlled evaporation	Polymer is dissolved in a solvent/non-solvent mixture. Evaporation of solvent during evaporation shifts the composition to a higher non-solvent and polymer content. This leads to polymer precipitation and the formation of a skin on the membrane.
Thermal precipitation	A polymer and solvent solution is cooled to enable phase separation. Evaporation of solvent can allow the formation of a skinned membrane. Frequently used to prepare microfiltration membranes.
Immersion	A solution of polymer plus solvent is cast (on a support) and immersed in a coagulation bath. Precipitation occurs by the exchange of solvent and non-solvent in the coagulation bath.

in which the polymer is soluble at high temperatures, typically only 5°C below the polymer melting point of 320–340°C, while, at low temperatures, below 100°C, the polymer is only poorly soluble in the chosen solvent. Examples of suitable solvents, with a plurality of aromatic rings, are tetraphenyls, hexaphenyls or polar polyaromatic compounds. The initial concentration of the polymer in the solvent is 10–50 wt.% (preferably 20%); a pore-forming agent (e.g. an inorganic salt or soluble polymer) can be added to the solution. With pore diameters in the range 0.001–1 µm, the membranes manufactured in this way may be asymmetric or isotropic, and either unsupported or supported (e.g. on PTFE, carbon fibre or stainless steel).

Alternative solvents for these otherwise intractable polymers are certain very strong mineral acids, such as liquid hydrogen fluoride, trifluoromethane sulphonic acid and sulphuric acid. Casting solutions can be formed containing, for example, 7–14 wt.% of PEK in 98% sulphuric acid, to produce both flat sheet and hollow fibre membranes for ultrafiltration.

8.4.2 Manufacture of inorganic membranes

There is growing interest in the use of inorganic membranes because of their robustness, their tolerance to extreme conditions of operation, such as higher temperature and aggressive chemicals, and the resultant long life, which offsets their higher initial cost as compared with polymeric membranes. The materials include ceramics, metals, carbon and glass. Some examples are listed in Table 8.7. Inorganic membranes may be homogeneous, asymmetric or composites.

8.4.2.1 Ceramic membranes

Almost all ceramic membranes are made by the sintering of a layer of carefully sized particles. A layer so made would be far too brittle to survive separate use, so

Table 8.7 Range of available porous inorganic membranes

Membrane material	Support material	Membrane pore diameter (nm)	Geometry of membrane element
Ni, Au		> 500	Tube
Ag, Pt			
Ag/Pd		0	Tube
ZrO_2	C	4	Tube
ZrO_2	C	4–14	Tube
ZrO_2	Metal	Dynamic	Tube
ZrO_2	Al_2O_3	10	Tube
SiC	SiC	150–8000	Tube
SiO_2 (glass)		4–120	Tube capillary
Al_2O_3	Al_2O_3	4–5000	Monolith/tube
Al_2O_3	Al_2O_3	200–5000	Tube
Al_2O_3	Al_2O_3	200–5000	Tube
Al_2O_3	Al_2O_3	200	Tube
Al_2O_3	Al_2O_3	25–200	Disk

all ceramic membranes are manufactured as a composite structure, with the membrane layer laid down on a porous substrate before sintering.

Composites require a support of open structure, and they may be of ceramics or carbon. For ceramics these supports are typically tubes or monolithic elements with several channels, as in Figure 8.9, fabricated by ceramic shaping methods such as slip-casting, extruding, etc. Carbon supports are typically produced by pyrolysis of a polymeric precursor, or by the pressing of carbon powders or fibres. The supports typically have pore sizes in the range 5–15 μm and porosities of 40–50%, or greater for carbon supports.

Typical use of these supports is to produce microfiltration membranes, which have deposited layers 10–50 μm thick, with pores 0.2–1 μm in size, and 40–50% porosity. The membranes are prepared by film coating the porous support with a suspension of the ceramic powder. The thickness of the coated layer is adjusted by changing the viscosity of the suspension, for example by changing its solids content. In preparation, pinholes in the deposited layer are avoided by suppressing the capillary force effect in the pores. The membrane layer is then formed by sintering at high temperatures, e.g. 1200–1450°C for alumina, the temperature used depending upon material, powder particle size and required pore structure.

The suspensions used in the process are prepared either by milling the powders or, for finer suspensions, by hydrolysis of salts or alkoxides (e.g. those of aluminium, zirconium and silicon). Overall the method is used to apply layers having pore sizes from 0.05 to 0.5 μm and, in the case of zirconia, suspensions on carbon of 0.01 μm pore size. The use of colloidal suspensions is applied in the 'sol–gel' process, which uses the capillary forces in the support to improve adherence between membrane layer and support. The method produces a sharp pore size distribution, with rapid production of layers to 0.01 μm in thickness. In practice the support quality has to be very good and the pore size in the top of the support should be 1 μm or less, otherwise the capillary forces are too weak at the start of the cake filtration/slip casting process. The method can be used to produce membranes with multiple layers, the top layer being the thinnest and with the smallest pore size. Final pore sizes of the order of 0.003 μm can be produced in this way (see Figure 8.18).

The production of crack-free membrane layers requires careful control of the drying, calcining and sintering stages. Drying control agents and organic additives, to adjust viscosity, are frequently employed to adjust the pore size distribution. During calcination and sintering the additives are burnt out. Membranes produced by these methods include alumina and titania layers on ceramics and glass, zirconia on carbon and alumina, and silica on alumina.

Classical slip-casting of slurries or sols on ceramic supports is a common procedure for the preparation of commercial microfiltration and ultrafiltration materials. These materials are manufactured by association of various granular layers. Each ceramic layer is characterized by its thickness, porosity and mean pore diameter, and these parameters are controlled by the particle size and synthesis method. However, the experimental hydraulic resistance of an inorganic composite membrane can be much larger than that obtained by

summing the individual resistances of all the layers. This is explained by the existence of a transition boundary layer between two porous media having drastically different pore sizes.

Non-infiltrated ceramic membranes can provide the expected water permeabilities. To prepare non-infiltrated membranes a new step is introduced, this being pretreatment of the support by impregnating the top of the support material with an aqueous solution of methyl cellulose. After the resulting polymer film has dried, the ceramic suspension is poured into the tube, which is then evacuated for 10 minutes, during which the polymeric dense film prevents any penetration into the pores of the support. The subsequent firing operation destroys the polymeric film and leaves a non-infiltrated membrane. The final temperature and time of firing control the mean pore size and size distribution of the membrane. This process is well suited to the production of titania membranes.

8.4.2.2 Carbon membranes

Carbon membranes, as shown in Figure 8.19, are produced from a thin porous layer of carbon (approximately 0.01 µm thick) applied to the internal surface of a narrow diameter support tube made from a carbon fibre/carbon matrix. The active layer pore size is in a range of 0.1–1 µm. Carbon membranes are particularly useful for operation at very low pH and they can function at temperatures of 165°C and at pressures up to 40 bar. They are suitable for conditions when many cleaning cycles are required either by backflushing or chemically.

8.4.2.3 Porous glass

A technique for preparing porous glass membranes combines leaching with the thermal phase inversion process used for the production of certain types of polymeric membrane. A three-component mixture of the oxides of sodium, boron
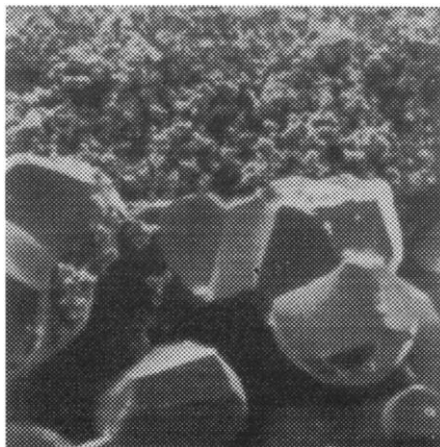

Figure 8.18. Scanning electron micrograph of a ceramic membrane.
(Photograph: APV Membrantechnologie GmbH).

and silicon is converted into a homogeneous melt. When this is cooled it separates into two phases. One phase consists mainly of insoluble silica, while the other phase is soluble. After solidification, the soluble phase is leached out by acid to produce a porous structure.

8.4.2.4 Metal membranes

There is a very indistinct boundary line in any classification of membrane media between ceramic and metal media. Most 'metal' membranes are actually a substrate of metal, with the oxide of that metal, i.e. a ceramic, forming the actual active layer at the surface of the membrane. However, it is customary to regard media that are mainly metal as metal membranes, and they are so discussed here, although there are one or two media that are all metal.

The first of these all metal media is the range of pure metallic *silver membrane* discs available from Osmonics Inc. These are in the form of discs of eight different diameters between 13 and 293 mm, and with particle retention ratings extending from 0.2 to 5 μm. Originally produced by the sintering of silver granules, these membranes are now formed by a reaction bonding mechanism that transforms a suspension of amorphous silver into a strong homogeneous crystalline network of porous silver. The membranes are 50 μm in thickness, with a 60% open area. They are claimed to be usually more economical than disposable filters because they can be reused several times after chemical or ignition cleaning.

Membrane media are also made from *anodized aluminium*. An asymmetric structure that can be formed by anodizing aluminium is shown schematically and photographically in Figure 8.20. The top-side pores have a size of approximately 0.025 μm, while the support pores are of the order of 0.2 μm.

During anodic oxidation, several metals develop coherent porous oxide coatings that adhere strongly to the metal substrate, limiting the direct use of the porous layer as a membrane. For example, anodizing aluminium in electrolytes of oxalic, phosphoric or sulphuric acid, generates a porous structure inwards from the outer surface only as far as an imperforate barrier layer. However, if the voltage of the anodizing cell is varied, say by reducing the starting potential from 25 V to zero in steps of 0.5 V, the resultant pore structure is altered; the single
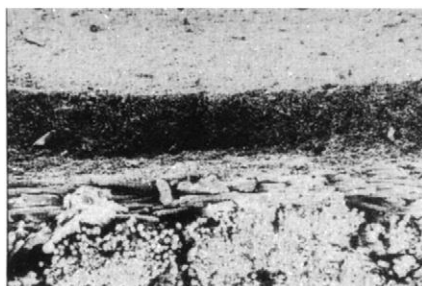

Figure 8.19. Photomicrograph of a carbon composite membrane showing the fine upper layer and the carbon fibre/composite support. (Photograph: Le Carbone Lorraine)

pores that normally form instead branch into numerous small pores that weaken the film near the substrate metal. Collectively, the branched pore system introduces a weakened stratum into the metal oxide film, thus enabling it to be quite easily separated from the substrate.

The barrier layer is very thin in this process and is generally left on the metal substrate. The detached oxide film is therefore porous on both sides. However, before it is detached from the metal substrate, a perforated supporting layer can be attached to the other side of the film by heat sealing or glue.

An inorganic membrane in the form of an *etched aluminium foil*, as shown in Figure 8.21, may be made from aluminium foil by an etching process that generates a capillary pore structure with a pore size of 0.5–8 μm. Recrystallized aluminium foil is etched, either on both sides to produce a symmetrical pore structure, or on one side to produce an asymmetric structure. The membrane has also been made with a silicon rubber coating, and also with a finer pore size, down to 0.002 μm, produced by coating the pore walls with alumina.

The following typical flow rates for the membrane are reported:

- air – 7000 $m^3/m^2/h$ bar;
- water – 1000–2000 $l/m^2/h$ bar;
- methanol – 2000–3000 $l/m^2/h$ bar.

Advantages claimed for aluminium foil membranes as compared with polymeric or ceramic membranes are:

1. the foil is easily formed; a laser-welded tubular format has been used for standard microfiltration tests;
2. it has excellent resistance to organic solvents, even at elevated temperatures, and to radiation;
3. it is stable in aqueous solution and withstands cleaning by bleaching with oxidizing agents;
4. it is electrically conducting, a property that has been used to obtain flux enhancement in microfiltration, and can facilitate cleaning; and
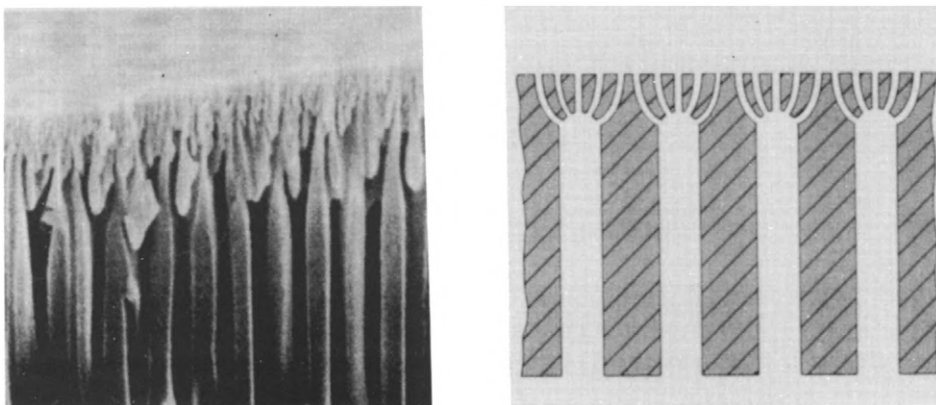

Figure 8.20. Anodized aluminium membrane with asymmetric support. (Photographs: Alcan Int. Ltd)

5.   it is tough, withstanding pressures up to 20 bar; this also allows increased filtration rates.

The main metal membrane, however, is that made from *sintered metal*, usually supported on a layer of sintered wire mesh. A simple example of this is Pall's Supramesh Z, data for which are included in Table 6.18 of Chapter 6. It combines a layer of sintered mesh, with a layer of powder or fibre sinter-bonded to the upper surface.

A sophisticated variant of this type of composite metal medium provides the basis for the Pall range of PMM metal membranes. These incorporate a thin sintered matrix of stainless steel or other metal powder within the pore structure of sintered woven wire mesh, as can be seen in the microphotograph of Figure 8.22. These thin, strong and ductile media can be pleated into high specific area packs, while the smooth and highly uniform surface functions as a high-performance medium for filtration down to 2 µm absolute with liquids and 0.4 µm with gases. Some relevant data are given in Table 8.8.

These PMM membrane media are also effective support layers in the highly robust multilayer elements used for filtering molten polymers, where the process conditions combine viscosities up to 4000 poise, temperatures of 250–350°C, and pressure differentials as high as 300 bar.

8.4.2.5 Organo-mineral membranes

Zirfon is a novel form of membrane material described by Leysen[9], which combines mineral particles with conventional polymeric materials. For example, zirconia particles are combined with polysulphone by dispersing them in the polymer solution used to cast membranes by immersion precipitation in a water bath. The resulting membrane structure consists of a porous polymer network
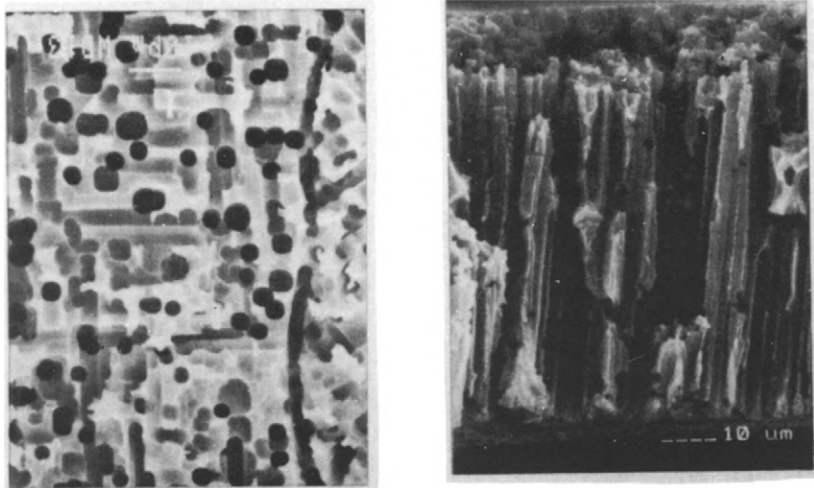
Figure 8.21. Etched aluminium foil membrane: (left) double-sided etched foil; (right) cross-section of the same double-sided etched foil.

incorporating the mineral grains, their presence significantly modifying the resulting membrane structure and the properties of the membrane surface in a very favourable manner. An increase in the weight percentage of zirconia in the casting solution significantly increases the membrane permeability and hence flux; the cut-off values of the membranes are around 25 kD, thus confirming that there are no significant changes in skin pore size.
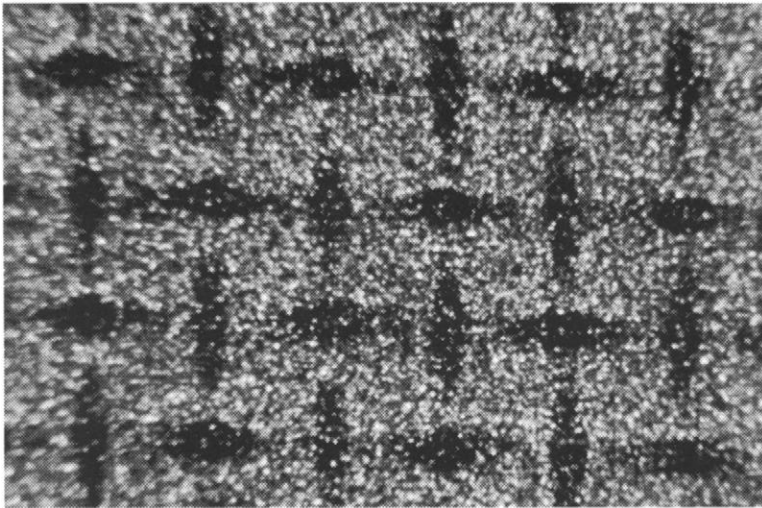
Figure 8.22. Pall 'PMM' filter medium is a sintered composite of mesh and powder.

Table 8.8   Pall PMM sintered mesh and powder media

Media grade	Micron removal rating					Nominal standard thickness (mm)	Permeability[c]	
	Liquid service[a]			Gas service[b]				
	90%	99%	100%	Wt.% removed	100%		to air	to water
M020	0.1	0.5	2	> 99.99	0.4	0.14	4.7	0.07
M050	0.6	2	5	99.99	0.6	0.14	7.6	0.12
M100	2	5	10	99.97	1.3	0.13	10	0.21
M150	5	9	15	99.96	2.5	0.15	31.8	0.35
M200	8	13	20	99.93	4.0	0.23	38.8	0.84
M250	10	16	25	99.90	9.0	0.23	152	2.95

[a] Using AC dusts in water, efficiency measured by particle count.
[b] Based on AC Fine Test Dust in air. Absolute retention rating based on particle count data.
[c] l/dm^2/min @ 10 mbar pressure drop.

The technology is employed by the Dutch company X-Flow to manufacture hollow fibre membranes for the filtration of potable water and wine. Flat sheet membranes for battery separators are also available.

8.5 Characterization of Membranes

Characterization methods for porous membranes can be divided into two groups of parameters: structure related and permeation related. Certain tests are also used to establish the integrity of membranes in specific applications. The direct measurement of pore statistics is routinely carried out by electron microscopy, as is seen in the various typical SEM (scanning electron microscopy) photographs of membrane structures in this chapter.

Table 8.9 summarizes various test procedures used for microfiltration and ultrafiltration membranes or for filters incorporating these membranes. It should be noted that the asymmetric structure of most ultrafiltration membranes, with top layer pore sizes in the range of 20–1000 Å, means that many of the methods of characterization of microfiltration membranes cannot be applied. Bubble point and mercury intrusion methods require high pressures that would damage or destroy the membrane structure; SEM is generally not possible and TEM (transmission electron microscopy) is not always applicable. The methods that can be used with ultrafiltration membranes include permeation experiments and methods such as gas adsorption–desorption, thermoporometry, permporometry and rejection measurements. The appropriate test methods are discussed in Chapter 11.

Table 8.9   Tests for characterizing membranes or membrane filters

Principle of test	Medium	Characteristic
Microfiltration membranes		
Air diffusion	Air	Integrity
Bubble point test	Air	Pore size
Cartridge retention test	Water	Filtration efficiency
Flow rate vs differential pressure	Water	
Particle shredding test	Water	
TOC tests	Water	
Resistivity test	Water	
Bacteria passage test	*Pseudomonas diminuta*	Sterility
Mercury intrusion test	Hg	Pore size and pore distribution
Latex sphere test	Latex sphere dispersion	Integrity
Water penetration test	Water	Integrity
Electron microscopy (SEM, TEM)		Pore size, shape, distribution, density
Permeation measurements		Water flux for pore size and distribution.
Ultrafiltration membranes		
Gas adsorption–desorption	N_2	Pore size and distribution
Thermoporometry	Water	Pore size and distribution
Permporometry	Gas	Pore size and distribution
Solute rejection	Various solutes	MWCO

8.6 Commercial Membranes

The performance of a membrane is defined in terms of two factors, fluid flux and selectivity. Ideally a membrane is required to combine high selectivity with high permeability, but typically attempts to maximize one factor often result in a reduction in the other. Membrane performance characteristics vary considerably from manufacturer to manufacturer, even where comparisons are between nominally identical materials. What follows here is a selection from the very wide range of membrane media available, the selection being made to highlight particular features of the membrane as a filter medium. The emphasis is primarily on microfiltration and ultrafiltration media, with reference to nanofiltration and reverse osmosis membranes only as necessary for completeness.

This part of the first edition's coverage of typical membrane media was divided into separate treatment of micro- and ultrafiltration. These two areas have merged significantly in the time since that edition was prepared, so the coverage now is very largely by material rather than membrane process.

8.6.1 Polymeric membranes

The specifications of Millipore's range of membrane microfilters, with pore sizes in the range 0.025–12 μm, are given in Table 8.10, while their contrasting surfaces are shown in the SEM photographs of Figure 8.13. Within this range it is possible to obtain variants of the basic materials. For example, Durapore PVDF is available as hydrophilic, hydrophobic or super hydrophobic membranes, with radically different protein binding characteristics. The track-etched Isopore polycarbonate membranes are also available in polyethylene terephthalate (PET), which is more resistant to organic solvents.

Certain of these membranes are supplied bonded to a suitable support. The Fluoropore PTFE membranes are laminated to high-density polyethylene to improve handling; however, certain pore grades are available as unsupported materials, where there is a risk of degradation of the support. These are recommended for the filtration of gases and non-aqueous liquids, although a hydrophilic material is available for the filtration of aqueous solutions. Membranes made from polypropylene (for sterilization applications) and PVC (for air monitoring) are also available.

Dead-end microfiltration is primarily carried out with flat sheet membranes, either as discs or rectangular sheets, or in the form of pleated cartridges that can incorporate several square metres of filtration area. Table 8.11 gives specifications for the sheet membranes Millipore provides for use in cross-flow modules of the type illustrated in Figure 8.23. Membranes are available in two materials, Durapore PVDF and Ceraflow, which is a ceramic of α-alumina; each material is available in two grades, a hydrophilic grade for microfiltration and a hydrophobic grade with finer pores for ultrafiltration.

A complete spectrum of membrane media, covering microfiltration to reverse osmosis is supplied by Osmonics, in a catalogue approaching 1000 pages (for

Table 8.10   Specifications of Millipore membranes

Specifications

Filter type	Mean pore size (μm)	Typical flow rate[a], water[b]	Typical flow rate[a], air[c]	Typical porosity (%)	Typical refractive index	Minimum bubble point[d] (bar)	Minimum bubble point[d] (psi)	Autoclavable	Mean thickness (μm)
Durapore (polyvinylidene difluoride)									
SVLP	5.0	288	–	70	1.42	0.21	3	Yes	125
DVPP	0.65	69	–	70	1.42	0.98	14	Yes	125
HVHP	0.45	35	6	75	1.42	0.56	8	Yes	125
HVLP	0.45	29	–	70	1.42	1.55	22	Yes	125
GVHP	0.22	15	3	75	1.42	1.20	17	Yes	125
GVWP	0.22	6.9	–	70	1.42	3.1	45	Yes	125
VVLP	0.10	2.5	–	70	1.42	4.9	70	Yes	125
MF-Millipore (mixed cellulose acetate and nitrate)									
SC	8.0	620	65	84	1.515	0.42	6	Yes	135
SM	5.0	580	32	84	1.495	0.42	6	Yes	135
SS	3.0	320	30	83	1.495	0.70	10	Yes	150
RA	1.2	270	20	82	1.512	0.77	11	Yes	150
AA	0.80	190	16	82	1.510	0.98	14	Yes	150
(black)		190	16	82	–	1.12	16	No	150
DA	0.65	140	9	81	1.510	1.20	17	Yes	150
HA	0.45	60	4	79	1.510	2.11	30	Yes	150
(black)		60	4	79	–	2.32	33	No	180
PH	0.30	32	3	77	1.510	2.46	35	Yes	150
GS	0.22	18	2	75	1.510	3.52	50	Yes	150
VC	0.10	1.5	0.4	74	1.500	14.1	200	Yes	105
VM	0.05	0.74	0.2	72	1.500	17.6	250	Yes	105
VS	0.025	0.15	0.15	70	1.500	21.1	300	Yes	105
Fluoropore (PTFE)									
FS	3.0	286	20	85	e	0.05	0.7	Yes	200
FA	1.0	90	16	85	e	0.21	3	Yes	145
FH	0.5	40	8	85	e	0.49	7	Yes	175
FG	0.2	15	3	70	e	0.91	13	Yes	175
Miltex (PTFE)									
LC	10.0	126	14	68	–	0.04	0.5	Yes	125
LS	5.0	51.9	9	60	–	0.06	0.9	Yes	125
Isopore (polycarbonate film)									
TM	5.0	2000	50	–	1.6	0.21	3	Yes	10
TS	3.0	1500	50	–	1.6	0.42	5	Yes	9
TT	2.0	350	22	–	1.6	0.63	9	Yes	10
RT	1.2	250	20	–	1.6	0.77	11	Yes	11

Table 8.10 (*continued*)

Specifications

Filter type	Mean pore size (μm)	Typical flow rate[a], water[b]	Typical flow rate[a], air[c]	Typical porosity (%)	Typical refractive index	Minimum bubble point[d] (bar)	Minimum bubble point[d] (psi)	Autoclavable	Mean thickness (μm)
AT	0.8	215	20	–	1.6	1.3	18	Yes	9
DT	0.6	115	10	–	1.6	1.7	24	Yes	10
HT	0.4	70	10	–	1.6	2.5	35	Yes	10
GT	0.2	7	1	–	1.6	5.3	75	Yes	10

[a]Flow rates listed are based on measurements with clean water and air, and represent initial flow rates for a liquid of 1 centipoise viscosity at the start of filtration, before filter plugging is detectable. Actual initial flow rates may vary from the average values given here.

[b]Water flow rates are millilitres per minute per cm^2 of filtration area, at 200°C with a differential pressure of 0.7 bar (10 psi). Flow rates for Fluoropore, Durapore hydrophobic and Miltex filters are based on methanol instead of water.

[c]Air flow rates are litres per minute per cm^2 of filtration area, at 20°C with a differential pressure of 0.7 bar (10 psi) and exit pressure of 1 atmosphere (14.7 psia).

[d]Bubble point pressure is the differential pressure required to force air through the pores of a water-wet filter (except methanol-wet for Fluoropore, hydrophobic Durapore and Miltex filters).

[e]Crystalline and amorphous regions of Fluoropore filters have differing refractive indices, and it is therefore not possible to obtain uniform clearing.

Additional notes: Flow rate correction for viscosity: For a liquid having a viscosity significantly different from that of water (1 cps), divide the water flow rate by the viscosity of the liquid in centipoises to obtain the approximate initial flow rate for the liquid in question (viscosity of methanol is 0.6 cps at 20°C).

Water Extractables: Water extractables measure 5% or less for most filter types, except for Durapore membranes, which measure 0.5%.

systems as well as elements and components). The microfiltration media are marketed under the Desal brand name, as spiral wound units, in three ranges, all safe up to 50°C:

- E500 Series: cut-off size 0.04 μm, made from polysulphone.

EW4026F	5.6 m² filter area	24.6 m³/day flow at 207 kPa & 25°C
EW4040F	8.4 m²	41.6 m³/day
EW8040F	32.5 m²	136.1 m³/day

- J Series: cut-off size 0.3 μm, made from PVDF.

JX4040F	8.4 m² filter area	45.4 m³/day flow at 207 kPa & 25°C
JX8040F	32.5 m²	151.0 m³/day

- K Series: cut-off sizes 0.1, 0.2, 0.5, 1.0 and 3.0 µm, made from PTFE.

K2540	1.2 m² filter area
K4040	4.7 m²
K8040	18.6 m²

Table 8.11   Millipore membranes for MF and UF cross-flow filtration

| Specification	Durapore	Ceraflo	PZHK	Ceraflo-UF
Material	Hydrophilic PVDF	α-Alumina with Teflon end seal	Hydrophobic PVDF	α-Alumina with Teflon end seal
Pore sizes (µm)	0.10 0.22 0.45	0.20 0.45 1.00	0.04 (approx.)	0.02 (approx.)
NMWL (kDalton)			200	50
Tested by	Bubble point	Bubble point	Dextran retention	Dextran retention
Properties				
Temperature	4–135°C	−100–150°C	4–135°C	−100–150°C
Max. pressure (25°C)	6 bar	10 bar	6 bar	10 bar
Continuous	2–10	0–14	2–12	4–10 (> 50°C)
Intermittent	1–13	0–14	1–13	4–10 (> 50°C)
Organic solvent compatibility	Limited	Broad	Limited	Broad
Protein binding	Very low	High	Medium	High
Biocompatibility USP test	Pass	n/a	Pass	n/a
Abrasion resistance	Poor	Excellent	Poor	Excellent
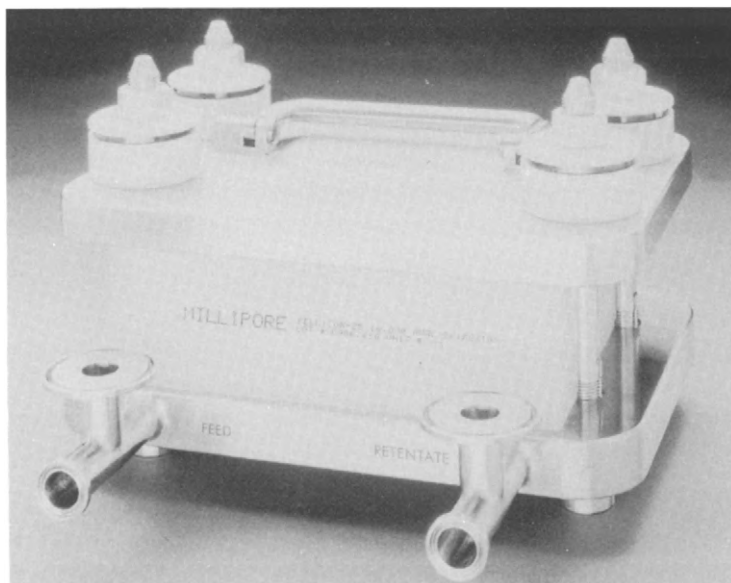
Figure 8.23. A 'Pellicon' cassette holder for cross-flow filtration. (Photograph: Millipore Corporation)

Whatman's ranges of track-etched microfiltration media are sold under the Nuclepore and Cyclopore brand names. Cyclopore in polycarbonate and polyester, Nuclepore in polycarbonate and mixed cellulose esters (CA and CN). Typical flux data and other values are given in Table 8.12 for the Nuclepore media. Cyclopore has a similar range of pore sizes (0.1–12 μm) and is slightly thicker (8–20 μm). Values of flux decrease with pore size and there is a corresponding increase in the bubble point pressures.

Common polymeric materials used for ultrafiltration membranes are regenerated cellulose and polysulphone or polyethersulphone, which are available in a range of molecular weight cut-off values, as illustrated by Millipore's media in Table 8.13.

Membrane area data for ultrafiltration hollow fibre cartridge units with polysulphone membranes are given in Table 8.14. These membranes have internal diameters between 0.5 and 1.5 μm and are free from macrovoids. For pure water, the cross-flow velocity will have little, if any, effect on flux. However, this is not the case with real process fluids, where the build-up of solutes at the membrane surface induces concentration polarization that reduces the flux.

The performance of an ultrafiltration membrane is defined in terms of its ability to retain molecules of a specific size, i.e. a rejection factor R, which is expressed as a number between 0 and 1 (or sometimes as a percentage). Values of rejection are not absolute values for any single membrane or solution, but depend upon conditions of operation, the concentration of the feed solution, the

Table 8.12   Track etched 'Nuclepore' microfiltration membranes[d]

Rated pore size (μm)	Rated pore density (pores/cm²)	Nominal wt. (mg/cm²)	Nominal thickness (μm)	Bubble point[c]		Typical flow rates	
				psi	bar	Water[a] (ml/min/cm²)	Air (l/min/cm²)
12.0	1×10^5	1.0	8	< 1	> 0.07	3000	85[b]
10.0	1×10^5	1.0	10	> 1	> 0.07	2500	65[b]
8.0	1×10^5	1.0	7	3	0.21	2000	40[b]
5.0	4×10^5	1.0	10	3	0.21	2000	55[b]
3.0	2×10^6	1.0	9	7	0.48	1500	50[b]
2.0	2×10^6	1.0	10	9	0.62	350	22
1.0	2×10^7	1.0	11	14	0.96	250	25
0.8	3×10^7	1.0	9	18	1.24	215	24
0.6	3×10^7	1.0	10	29	2.00	115	10
0.4	1×10^8	1.0	10	42	2.90	70	11
0.2	3×10^8	1.0	10	82	2.65	20	4.0
0.1	3×10^8	0.6	6	> 100	> 6.90	4.0	1.5
0.05	6×10^8	0.6	6	> 100	> 6.90	0.7	0.70
0.015	6×10^8	0.6	6	> 100	> 6.90	< 0.01	0.024

[a]   Typical flow rate using water or air at 10 psi (0.7 bar).
[b]   5 psi (0.35 bar).
[c]   Water bubble point.
[d]   Whatman International Ltd.

flow rate and the extent of concentration polarization at the membrane surface. Rejection coefficients vary with the molar mass of the solute, as shown in Figure 8.24 for the ultrafiltration of dextran and with the membranes of Table 8.13. The use of polydisperse dextran solutions is claimed to be a better retention test marker than single-protein solutions, to ensure quality control of the rejection performance.

The tubular membranes illustrated in Figure 8.7 are the basis for PCI Memtech's range of RO, NF and UF separation systems, which have now been extended to cover microfiltration, while the types supplied now include spiral wound modules as well as ceramic tubes. There are 22 items in the tubular membrane range, covering reverse osmosis, nano- and ultrafiltration, and 9 items in the spiral wound list.

An ultrafiltration specialist, Koch Membrane Systems, has, for just industrial water and wastewater treatment, 10 different systems, all covering cut-off figures of 50–120 kD. There are three tubular formats, in PVDF, four hollow fibre formats, variously in PAN and polysulphone, and three spiral wound, also in PVDF.

A/G Technology is a hollow fibre specialist, providing membranes and membrane systems for microfiltration and ultrafiltration. The microfiltration cartridges have pore cut-off sizes of 0.1, 0.2, 0.45 and 0.65 μm, while the ultrafiltration cartridges have nominal molecular weight cut-off (NMWC) values of 1000–750 000. Membrane areas run from less than 0.01–28 m².

Table 8.13   Millipore membranes for ultrafiltration[b]

Specifications	PL series	PT series
Material	Regenerated cellulose on polypropylene	Polyethersulphone on polypropylene
	NMWL (kD)	1 PLAC
	3 PLBC	
	5 PLCC	10 PTGC
	10 PLGC	30 PTTK
	30 PLTK	50 PTQK
	100 PLHK	100 PTHK
	300 PLMK	300 PTMK
Retention specifications	See Figure 8.24	See Figure 8.24
Properties		
Temperature	4–50°C	4–50°C
Maximum pressure	7 bar	7 bar
pH range (25°C)		
Continuous	2–12	1–14
Intermittent (e.g. cleaning)	2–13	1–14
Organic solvent compatibility	Broad[a]	Limited
Protein binding	Very low	High
Susceptibility to antifoam fouling	Low	High

[a]   In Prostak-UF modules only.
[b]   Millipore Corporation.

Table 8.14   Membrane area values for UF polysulphone membranes

Membrane area as a function of housing and fibre/tubule internal diameter

Cartridge housing identifier	Fibre/tubule internal diameter code	Fibre/tubule internal diameter (mm)	Cartridge membrane area	
			sq. ft	sq. m
	C	0.5	0.16	0.015
3	D	0.75	0.10	0.009
	E	1	0.08	0.007
	C	0.5	0.70	0.065
4	D	0.75	0.50	0.046
	E	1	0.35	0.032
4X2TC	H	2	0.8	0.073
	K	3	0.5	0.046
	C	0.5	3	0.28
5	D	0.75	2	0.19
	E	1	1.5	0.14
	C	0.5	6	0.56
	D	0.75	4	0.37
6	E	1	3	0.28
	H	2	2.4	0.22
	K	3	1.6	0.15
	C	0.5	6.7	0.62
8	D	0.75	5	0.46
	E	1	3.75	0.35
	C	0.5	15	1.4
	D	0.75	10	0.93
9	E	1	7.5	0.7
	H	2	6	0.55
	K	3	4.9	0.45
10	H	2	12.1	1.1
	K	3	8.8	0.82
	C	0.5	14	1.3
35, 35A	D	0.75	11	1
35STM	E	1	8.5	0.8
	C	0.5	36	3.4
55, 55A	D	0.75	27	2.5
55R,	E	1	23	2.1
55STM	H	2	14	1.3
	K	3	10.6	1
	C	0.5	65	6
75, 75R	E	1	40	3.7
	H	2	27	2.5
	K	3	20	2

Aided by the well-known non-stick properties of PTFE, the membranes made from ePTFE have proved to be highly successful, especially for use in fabric dust filters, using all kinds of cleaning mechanism: shaker, reverse flow or pulse jet. Versions are available utilizing a variety of substrate materials to suit different operating temperatures, as illustrated by the Tetratex media of Tables 8.15 and 8.16.

The use of ePTFE laminated fabrics in dust filters is beneficial by comparison with conventional fabrics in terms of air/cloth ratio (flow per unit area), pressure drop, bag life, and lower dust emission values. Several case histories are summarized in Table 8.17.

W L Gore, the originators of ePTFE, has recently introduced a new form of Gore-Tex ePTFE membrane, which, laid on a polyester needlefelt, is being marketed as a High Durability filter bag. The company also has a membrane medium offering catalytic destruction of dioxins and furans, and has established the Pristyne brand name for a series of filter bags using ePTFE membranes on substrates made from seven different fibres, as felts, wovens or spunbonds.

Dow is one of the largest membrane material makers in the world, largely for the reverse osmosis market, under the Filmtec brand name. Data for water treatment using these polyamide membranes are given in Table 8.18.

8.6.2 Inorganic membranes

In high-temperature processes with hot aggressive fluids, filtration requirements can only be met by a limited number of materials. Carbon is one such material well known for its corrosion resistance. Membranes made from carbon are typically a composite structure of a very thin layer of porous carbon applied to the internal surface of a narrow diameter carbon fibre/composite support tube. The membrane tubes are assembled in monolithic joint-free bundles (see Figure 8.25) using a carbon composite tube sheet. The bundles are then mounted in a shell made from an appropriate compatible material such as PTFE-lined steel or stainless steel. The carbon tubes are 6 mm internal diameter and 1.5 mm thick, giving good mechanical resistance, i.e. bursting pressures of 40 bar.
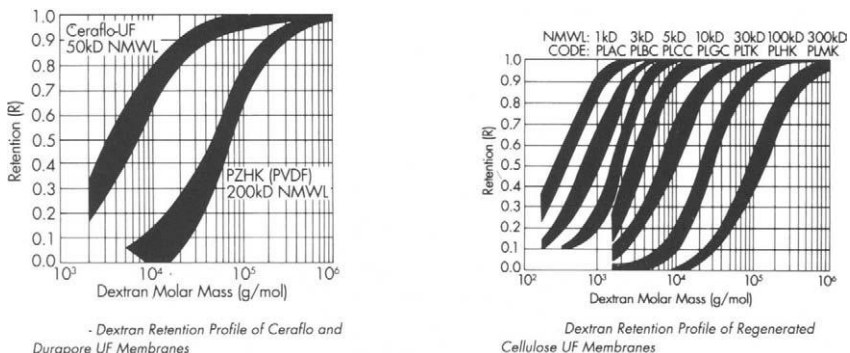

- Dextran Retention Profile of Ceraflo and Durapore UF Membranes

Dextran Retention Profile of Regenerated Cellulose UF Membranes

Figure 8.24. Rejection characteristics of the UF membranes in Tables 8.11 and 8.13.

Table 8.15 'Tetratex' PTFE membrane/needle felt laminates[a]

Product code	6202	6211	6212	6222	6272	6232	6242	6262
Fibre	PE	PE	PE	PP	$PE_{Epitropic}$	P-84	Nomex	Ryton
Scrim	PE	None	PE	PP	PE	P-84	Nomex	Ryton
Weight (g/m^2)	400–490	510–590	510–590	490–560	440–520	440–520	440–520	510–560
Thickness (mm ± 0.25)	1.1	1.5	1.5	1.8	1.3	2.3	1.4	1.5
Width (mm ± 12.5)	1690	1690	1690	1690	1690	1730	1730	1690
Air permeability ($1/dm^2$/min @ 20 mm WG)	39–54	39–54	39–54	39–54	39–54	39–54	39–54	39–54
Continuous service temperature (°C)	135	135	135	120	135	245	205	190
Minimum Mullen burst pressure (kg/cm^2)	25	32	32	35	32	25	28	28
Minimum breaking strength (kg/5 cm)								
Machine direction	27	34	34	36	34	67	54	45
Across machine	54	67	67	45	67	101	76	45
Maximum elongation (% @ 23 kg/5 cm)								
Machine direction	10	8	8	8	10	n/a	n/a	8
Across machine	10	8	8	8	10	n/a	n/a	8
Maximum % unrestricted shrinkage in 24 h,	3	3	3	3	3	1.5	2	3
dry heat @ specified °C	177	177	177	105	177	1 h @ 245	1 h @ 230	1 h @ 205

[a] Donaldson Tetratec.

This carbon tube module has a great tolerance to the many thousands of back flushing operations at 8–12 bar typically used to clean the membrane of fouling layers *in situ*. Sealing of the bundles into the end plates ensures no bypass problems. The membranes are tolerant to strong acids at all concentrations, hot organic solvents and alkaline baths, but not to strong oxidizing agents. Carbon is a fully biocompatible material, recommended for alimentary and other biological fluids.

In recent years, there has been substantial development of ceramic membranes, with specific features of heat resistance, a high degree of resistance to organic solvents, good cleaning potential, high mechanical strength, applicable in a wide pH range, a long life cycle and a good price/performance ratio. Modules are supplied in a wide range of sizes to meet most applications of microfiltration with a pore size of 0.1–5 μm. The filtration systems are constructed as cylinders equipped with ceramic filtration tubes. The disadvantages of ceramic membranes compared to polymeric membranes are that they are brittle, the surface area/volume ratio is lower and the cost is relatively high.

Typical characteristics of ceramic membranes are shown in Table 8.19. Ceramic ultrafiltration membranes can be constructed in several layers, by successively depositing finer layers of α- and γ-alumina onto a ceramics support tube of high porosity. The top layer is the real membrane layer and is responsible for the separation; it needs to be very thin to achieve a high flux. Sizes start from a membrane area of 0.05 m² with typical filtration flows of 3–9 dm³/h, up to a membrane area of 4 m² at filtration flows of 175–500 dm³/h. The configuration is based on a porous hexagonal log into which a series of 4 mm diameter channels are introduced. The elements are either single- or 19-channel design, with the latter giving a 0.2 m² internal filtration surface for a 900 mm long, 25 mm diameter unit. The operating range of pH is 1–11 at 700°C and 1–14 at 250°C. For microfiltration the pore size cut-off sizes can vary from 0.05 to 10 μm. Typical water fluxes are shown in Figure 8.26 for microfiltration membranes.

Table 8.16　'Tetratex' PTFE membrane/woven glass laminates[a]

Product code	6254	6253	6252	6255
Average weight (g/m²)	305	475	543	760
Actual weight (g/m²)	322–373	458–526	543–627	712–814
Width (mm ± 12.5)	978	978	1650	1650
BGF style no.	427	454	448	477
Finish style no.	615	615	615	615
JPS style no.	3602	651	648	7577
Finish style no.	Teflon B	Teflon B	Teflon B	Teflon B
Air permeability (l/dm²/min @ 20 mm WG)	34–44	29–39	24–34	29–39
Continuous service temperature (°C)	260	260	260	260
Minimum Mullen burst pressure (kg/cm)²	35	42	42	63
Minimum tensile strength (kg/5 cm)				
Machine direction	260	450	270	450
Across machine	144	225	225	315

[a]　Donaldson Tetratec.

Table 8.17   Case histories demonstrating benefits of PTFE laminates for dust filters[a]

Dust:	PVC		Lead oxide		Sugar		Boiler flyash		Cement	
System:	Spray dryer		Processing		Silo exhaust		Exhaust gases		Crusher venting	
Filter type:	Reverse air		Shaker		Pulse jet		Shaker		Reverse air + shaker	
Filter media:	Acrylic	GoreTex	Dacron	GoreTex	Egg-shell polyester	GoreTex	Silicone cotton	GoreTex	Polyester felt	GoreTex
Air/cloth ratio	2/1	3.6/1	1.5/1	3/1	10/1	10/1	7/1	7/1	5/1	5/1
Gas flow (m^3/min)	840	1540	616	1232	NA	22	NA	294	NA	266
Pressure loss (mm WG)	279	51	76	76	254	25	203	102	178	64
Bag life (months)	6	24	12	26	1/2	12	3	15	6	17
Comments		[b]	[c]				Visible plume	No plume visible		5 μm dust

[a]   W.L. Gore & Associates, Inc.
[b]   Up to 75% increase in production rate (kg/h).
[c]   At A/C ratio of 3/1, pressure loss > 300 mm WG.

The LCI Corporation sells what is basically a stainless steel tubular microfiltration system, which has a fine sintered TiO_2 membrane on a stainless steel support. For ultrafiltration, a ceramic membrane is laid on top of the titania, and for nanofiltration, a synthetic polymer membrane is laid on top of the ceramic one. The resultant separations achieved run from 1 μm down to 0.001 μm.

A fully metallic membrane is offered by GKN Sinter Metal Filters, in the form of its SIKA-R...AS medium. This involves powder metal technology to produce a base of coarse metal powder, and a thin layer (200 μm) of the same alloy diffusion bonded to it, during the sintering process. Operation up to 900°C in an oxidizing atmosphere is possible[10], with efficient removal of dust particles in the 0/5–10 μm range.

8.7 Guidance on Membrane Selection

The performance and selection of a membrane is affected by a multiplicity of factors associated with the membrane medium, the particulate material, the fluid carrier phase, the conditions of operation, and the interactions among all these

Table 8.18   Filmtec nanofiltration membranes[e]

Grade	Diameter[a]	Area[b]	Flow[c]	Rejection[d]
NF90-2540	61	2.6	2.3	99.0 (Mg SO$_4$)
NF90-4040	99	7.6	7.0	99.0 (Mg SO$_4$)
NF90-400	201	37.2	28.4	85–95 (NaCl)
NF200-400	201	37.2	30.3	35–50 (CaCl$_2$)
NF270-400	201	37.2	55.6	40–60 (CaCl$_2$)
NF270-2540	61	2.6	3.2	99.0 (Mg SO$_4$)
NF270-4040	99	7.6	9.5	99.0 (Mg SO$_4$)
NF400	201	37.2	25.7	98.0 (Mg SO$_4$)

[a]   Element diameter (mm) for 1016 mm length.

[b]   Separation area (m^2).

[c]   Water flow (m^3/day).

[d]   Stabilized flow rejection (%).

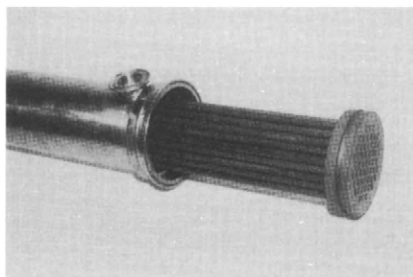[e]   The Dow Chemical Company.

Figure 8.25. Carbon fibre cross-flow filtration module.

Table 8.19   Characteristics of ceramic membranes

Product characteristics	Microfilter	Ultrafilter	Ultrafilter
Membrane composition	Alpha Alumina	Gamma Alumina	Zirconia Alumina
Available pore size	0.2–5 μm	50–1000 A	200–1000 A
Burst pressure	Limited by the maximum housing operating pressure		
Maximum operating pressure	120 psig (standard, higher pressures optional)	120psig (standard, higher pressures optional)	120psig (standard, higher pressures optional)
Water permeability 20°C			
0.2 μm pore Ø	2000 l/h m² bar		
40 A⁵ pore Ø		10 l/h m² bar	
500 A⁵ pore Ø			850 l/h m² bar
Resistance to corrosion	Can be washed with NaOCl 2% NaOH 2% HNO₃	Limited	Same as Microfilter
Steam sterilizable[a]	Yes	Yes	Yes

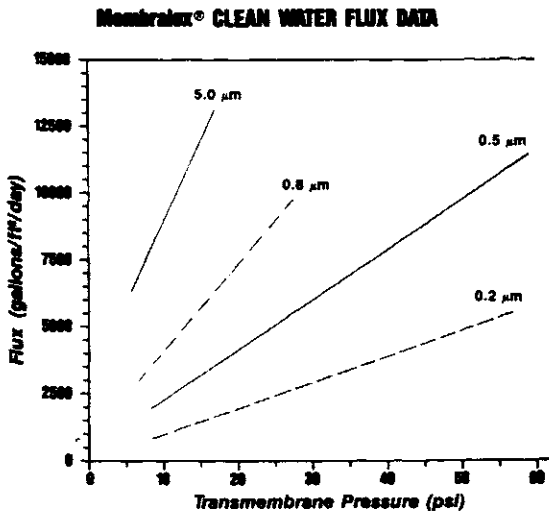[a]   The Membralox Steam Sterilization Procedure must be followed.

Figure 8.26. Typical clean water flux/pressure curves for ceramic membranes.

factors. Of particular importance are those that relate to the particulate material (size, shape, concentration, distribution, zeta potential, and whether it is inert or viable), the membrane structure (pore size, rating, asymmetry), the stability of the membrane (chemical, mechanical, thermal, hydrolytic, extractables, shedding), and the retention mechanisms (absorption, adsorption, impingement, cake retention).

The selection of an optimum (or at least an appropriate) membrane and system will usually require a trade-off between various possible alternatives. Table 8.20 summarizes the typical information required to permit a systematic analysis of the available options.

The important performance indicator in microfiltration is the volumetric flow through the membrane, which is directly proportional to the applied pressure difference across it. For most membranes, values of fluid flux are quoted for particular conditions of temperature and applied pressure, with specific fluids, which typically are water, air and methanol.

From the data normally available for membranes, it is possible to calculate the permeability constant for the membrane for a particular fluid. In principle, this should be independent of the fluid if there are no interactions between the membrane and the feed slurry. The important factor in microfiltration is not the flux of clean fluid but the performance during actual filtration. Performance is potentially affected by several solute-related parameters and specifically by concentration polarization and fouling.

A good general review of microfiltration is given in Table 8.21. This was produced originally by Costar, but is still generally applicable.

Microfiltration membranes are routinely used in a range of analytical procedures to determine particulate contamination in a wide range of gases and liquids. The procedures include the detection of micro-organisms in a variety of waters and process fluids (foods, beverages, pharmaceuticals) where the membrane traps the micro-organism and is subsequently used as the culture medium, in passive cell growth studies and in so-called blotting applications. A range of different types of membrane is used, including:

1.   mixed cellulose esters – e.g. biologically inert mixtures of cellulose acetate and cellulose nitrate; suitable for a wide range of analytical procedures, including gravimetric analysis by the ashing technique and light microscopy;

2.   PTFE – either unlaminated or laminated to a support of high-density polyethylene or polypropylene; for applications with gases and non-aqueous fluids, with acids and alkalis, and for higher temperature operation;

3.   silver – ideal collection medium for analysis of crystalline silica by X-ray diffusion and for the analysis of organics;

4.   PVDF – suitable for aqueous or organic samples; and

5.   track-etched polycarbonate – recommended for scanning and transmission electron microscopy.

Commercial polymeric ultrafiltration membranes are designed to give the requirement of high permeability and high permselectivity. An extensive range of membrane materials is used including polysulphone, polyethersulphone, PAN, polyimide, cellulose acetate, aliphatic polyamides, the oxides of zirconium

Table 8.20   Membrane filtration selection criteria

Criteria	Characteristics
Fluid properties	What liquid or gas is being filtered? What are the fluid properties (pH, viscosity, temperature, surface tension, stability, etc.)? What are the important chemical components and their concentrations? What pretreatment has been given to fluid? What is the desired minimum and maximum flow rate? What is the product batch size?
Pressure characteristics	What is the maximum inlet pressure? What is the maximum allowable differential pressure? Is there a required initial differential pressure? What is the source of pressure (centrifugal/positive displacement pump, gravity, vacuum, compressed gas, etc.)?
Sterilization/sanitization	Will the filtration system be steamed or autoclaved? Will the system be sanitized with chemicals or hot water? How many times will the system be sterilized or sanitized? What are the sterilized/sanitized conditions?
Hardware	Is there a restriction on the material for the housing? Is there a recommended housing surface finish? What are the inlet and outlet plumbing connections? Is there a size or weight restriction?
Filter	What is the size of particles to be retained? Will the filter be integrity tested; if so, how? Will this be a sterilizing filtration? Is there a minimum acceptable level of particle removal? Is there a recommended filter change frequency?
Temperature	What is the temperature of the fluid? Temperature affects the viscosity of liquids, the volume of gases and the compatibility of the filtration system.
Configuration	How will the filtration systems be configured – in series or in parallel? *Parallel flow arrangement*: uses several filters of equal pore size simultaneously to either increase flow rates, extend filter service life or lower differential pressure. It also permits filter changeout without system shutdown. The total flow rate and differential pressure is equally distributed across each filter. For any given flow rate, the differential pressure can be reduced by increasing the number of filters in parallel. *Series flow arrangement*: uses a group of filters of descending pore sizes to protect the final filter when the contaminant size distribution indicates a wide range or a high level of particulates that are larger than the final pore size. You can also use additional filters of the same pore size in series to improve particle removal efficiency, to protect against the possible failure of a unit within the system, and to add an extra measure of safety in any application.

Table 8.21   Guidance on membrane applications

Application	Recommended filter media			References/comments
	Description	Pore size (μm)	Diameter (mm)	
Air pollution analysis				
Asbestos, airborne	Mixed esters of cellulose	0.45, 0.8, 1.2	25	NIOSH Methods 7400 and 7402: EPA-CFR763-Fed Reg. 1987, pp. 41826–41905.
Cadmium	Mixed-esters of cellulose	0.8	37	NIOSH Method 7048
Carbon black	PVC	5.0	37	NIOSH Method 5000
Cyanides	Mixed-esters of cellulose	0.8	37	NIOSH Method 7904
Lead	Mixed-esters of cellulose	0.8	37	NIOSH Method 7082
Lead sulphide	PVC	5.0	37	NIOSH Method 7505
Nuisance dust	PVC	5.0	37	NIOSH Methods 0500 and 0600
Quartz in coal dust	Mixed-esters of cellulose	0.8	37	NIOSH Method 7602
Silica, crystalline	PVC	5.0	37	NIOSH Method 7601
Welding and brazing fume	Mixed-esters of cellulose	0.8	37	NIOSH Method 7200
Zinc oxide	PVC	0.8	25	NIOSH Method 7502
Trace elements	Polycarbonate aerosol-type	0.2–8.0	25–47, 8×10 in	Low trace metal contamination (Br, Pb, Zn, etc.) with aerosol holders
Bacterial Analysis				
Total coliform count	Mixed-esters of cellulose	0.45	47	*Standard Methods/Water & Wastewater, 17th Ed., 9222B*
Fecal coliform	Mixed-esters of cellulose	0.7	47	*Standard Methods/Water & Wastewater 17th Ed., 9221*
Legionella	Polycarbonate	0.2	37, 47	
Heterotrophic plate count (HPC) (formally known as standard plate count)	Mixed-esters of cellulose	0.45	47	*Standard Methods/Water & Wastewater, 17th Ed., 9215D*
Direct total microbial count	Polycarbonate . Mixed-esters of cellulose	0.2 5.0	25 25	*Standard Methods/Water & Wastewater, 17th Ed., 9216B*
Escherichia coli	Mixed-esters of cellulose	0.45	85	For *E. coli*, use REC-85® food micro membrane, direct plating technique in petri dish
Yeast and moulds	Mixed-esters of cellulose	0.65–1.2	13–47	
	Polycarbonate	0.6, 0.8	13–47	

Table 8.21 (*continued*)

Application	Recommended filter media			References/comments
	Description	Pore size (µm)	Diameter (mm)	
Sterility testing	Mixed-esters of cellulose	0.22, 0.45	47	For sterility testing, use gridded, sterile hydrophobic edge membranes (see *Code of Federal Regulations*, Title 21 #436)
Blood filtration				
RBC deformability	Polycarbonate Hema-Fil	4.7–5.0	13.25	
Plasmapheresis	Polycarbonate	0.6–1.0	90	Use fluid cross-flow, thin channel technique
Cell culture	Polycarbonate	0.4–3.0	13–47	Fit membrane to petri dish or culture plate
Chemotaxis				
Epithelial, fibroblasts, neutrophils, polymorpho-nuclear leukocytes	Polycarbonate (chemotaxis membrane, PVP-free)	2.0–8.0	13	For chemotaxis, use blind well or modified Boyden chambers
Macrophage	Polycarbonate (chemotaxis membrane)	2.0–8.0	13	
Cytology				
Cytopreparative and cyto-diagnostic methods	Polycarbonate, mixed-esters of cellulose	2.0–8.0	25.47	Use with Swin-Lok holder or vacuum filtration
		3.0—5.0	19×42	
EPA testing				
EPA toxicity characteristic leaching procedure (TCLP)	Glass fibre	0.7	90, 142	EPA Ref. 40CFR Part 268 Fed. Reg. 53:18795 May 24, 1988
Fuel testing	Mixed-esters of cellulose	0.45, 0.8	47	ASTM D2276
	Fuel monitor	0.8	37	
General filtration				
General clarification or prefiltration	Mixed-esters of cellulose	0.8–5.0	13–293	
	Glass fibre	D49, D59, D79	13–293	
Beverage stabilization	Mixed-esters of cellulose	0.45–1.2	47–293	
Particulate removal	Polycarbonate	0.1–5.0	13–293	
	Mixed esters of cellulose	0.1–5.0	13–293	
	Glass fibre (D49, D59, D79, 0.7 nominal)		10–293	

Table 8.21 (*continued*)

Application	Recommended filter media			References/comments
	Description	Pore size (μm)	Diameter (mm)	
Fine aqueous clarification	Polycarbonate	0.6–1.0	13–293	
	Mixed-esters of cellulose	0.65–1.2	13–293	
Bacterial removal	Mixed-esters of cellulose	0.22–0.45	13–293	
Adsorbable organic halogens (AOX)	Polycarbonate	AOX[R]	25, 47	
Alkaline elution, DNA	Polycarbonate	0.8, 2.0	25, 47	PORETRAITS[R] (NUCLEPORE[R]) Winter 1988
Forensic analysis	Polycarbonate	0.4	13	Sample collection for S.E.M.
Liposome extrusion	Polycarbonate	0.1–0.4	25–76	Use with high-pressure holder
HPLC solvent purification				
Samples, aqueous	Mixed-esters of cellulose	0.45	13, 25	
Samples, organic	PTFE	0.45	4–25	
Solvents	PTFE	0.45	47	
Parasitology				
Microfilariae (*Dirofilaria immitis*)	Polycarbonate	5.0	2.5	Use Swin-Lok holder or stainless steel syringe holder
Schistosoma haematobium	Polycarbonate	12.0	13	
Pharmaceuticals (human or veterinary)				
Small volume parenterals	Syrfil[R]-MF	0.22	25	
Prefiltration	Glass fibre	D49–D79	10–293	Parenteral processing must conform with FDA GMPs; 21 CFR 210 and 211
Sterilization	Mixed-esters of cellulose	0.22	13–293	
Protein or virus assay and purification				
Fractionation or collection	Polycarbonate	0.015–0.1	25–293	For protein or virus filtration, use Stirred Cell Series – S25, S43, S76 Swin-Lock® holders, or stainless steel holders
Purification	Polycarbonate	0.015–0.4	25–293	
Colony hybridization	Mixed-esters of cellulose	0.45	25, 85	
Low binding	Polycarbonate	0.4	25	
Serum filtration				
Prefiltration	Glass fibre	D49–D79	10–293	
	Mixed-esters of cellulose	0.3–1.2	13–293	

Table 8.21 (continued)

Application	Recommended filter media			References/comments
	Description	Pore size (μm)	Diameter (mm)	
Bacterial removal	Mixed-esters of cellulose	0.1–0.22. 0.45	13–293	
Mycoplasma removal	Mixed-esters of cellulose	0.1	13–293	
Sterilizing filtration				
Air venting	Syrfil*-FN (PTFE)	0.2	25. 50	
Fluids-aqueous	Mixed-esters of cellulose	0.22. 0.45	90–293	
Air or gas	PTFE	0.2	25–293	
Tissue culture media filtration				
Prefiltration	Glass fibre	D49	47–293	
	Mixed-esters of cellulose	0.1	4–293	
Bacterial removal	Mixed-esters of cellulose	0.22	90–293	
Mycoplasma removal	Mixed-esters of cellulose	0.1	90–293	
Water microbiology				
Escherichia coli	Mixed-esters of cellulose	0.45	47	*Standard Methods/Water and Wastewater*. 17th Ed.. 9260F
Fecal coliform	Mixed-esters of cellulose	0.7	47	*Standard Methods/Water and Wastewater*. 17th Ed.. 9222D
Fecal streptococcus	Mixed-esters of cellulose	0.45	47	*Standard Methods/Water and Wastewater*. 17th Ed.. 9230C
Fine particles	Mixed-esters of cellulose	0.45	47	
Giardia lamblia	Polycarbonate	5.0	293	Cyst Concentration and Analysis. EPA 600/S2-85/027 Sem. 1985
Leptospires	Mixed-esters of cellulose	0.45	13. 25	*Standard Methods/Water and Wastewater*. 17th Ed.. 9260I
Phytoplankton	Mixed-esters of cellulose	1.2–5.0	47	*Standard Methods/Water and Wastewater*. 17th Ed.. 10200C
Heterotrophic plate count (HPC) – formerly standard	Mixed-esters of cellulose	0.45	47	*Standard Methods/Water and Wastewater*. 17th Ed..
Salmonella	Mixed-esters of cellulose	0.45 0.45	142 47	*Standard Methods/Water and Wastewater*. 17th Ed.. 9260B

Table 8.21 *(continued)*

Application	Recommended filter media			References/comments
	Description	Pore size (µm)	Diameter (mm)	
Suspended particulates	Mixed-esters of cellulose	1.2–5.0	47	
	Polycarbonate	1.0–5.0	47	
	Glass fibre	0.7 nom	47	
Direct total microbial count	Polycarbonate	0.2	25	*Standard Methods/Water and*
	Mixed-esters of cellulose	5.0	25	*Wastewater,* 17th Ed., 9216B
Total coliform count	Mixed-esters of cellulose	0.45	47	*Standard Methods/Water and Wastewater,* 17th Ed., 9222B
Vibrio cholerae	Mixed-esters of cellulose	0.45	142	*Standard Methods/Water and Wastewater,* 17th Ed., 9260H
Virus concentration	Mixed-esters of cellulose	0.45	47, 90	*Standard Methods, Water and Wastewater,* 17th Ed., 9510B
	Glass fibre, D49		142	

and aluminium, and other ceramics. Membranes are produced as flat sheets, also used as spiral wound modules, and in tubular or hollow fibre forms.

The flux of the liquid through ultrafiltration membranes is much smaller than through microfiltration membranes, in the general range of 0.1–10 m^3/day, the actual figure depending upon many structural parameters. For pure water (or other liquids) there is a linear correspondence between flux and transmembrane pressure. With solutions there is a tendency for the flux to reach an asymptotic value with increasing pressure. This is a result of several factors, including concentration polarization, gelation, fouling and osmotic effects.

The selection of a membrane for ultrafiltration will require determining the molar mass of the species to be separated and selecting a membrane with a limiting rejection ($R \approx 1.0$) under anticipated conditions of operation. Small-scale application tests will generally need to be performed. Ultrafiltration membranes are rated in terms of their nominal molecular weight cut-off (NMWC). There are no industry-wide standards for this rating, hence manufacturers use different criteria for assigning ultrafiltration pore sizes. For example, for the concentration of protein, the protein should be larger than the NMWC of the membrane by a factor of 2–5. The greater the difference (i.e. the tighter the membrane pore size), the higher the protein yield. The protein shape, in addition to its molecular weight, plays a role in determining its retention by the membrane. The more globular the protein, the greater its retention, while linear
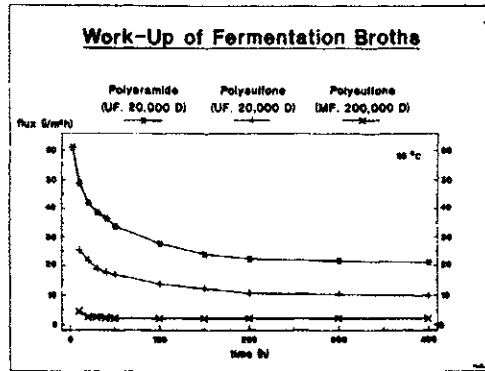
Figure 8.27. Variation of UF flux with conversion of a fermentation broth.

proteins may require a tighter membrane for high recoveries. Moreover, protein shape may be affected by solution pH or salinity.

Figure 8.27 shows the typical effect of time on the concentration of a fermentation broth with two types of ultrafiltration membrane, respectively hydrophilic polysulphone and polyaramid. Typically, the initial loss of flux is relatively rapid, whilst for longer times the decline in flux is less severe. The difference in the membrane flux behaviour is due to the greater tolerance of the very hydrophilic polyaramid membrane to fouling.

Although the separation mechanism of ultrafiltration is broadly considered to be one of sieving, in practice the effect of concentration polarization limits the flux, due to a build-up of solute in the concentration boundary layer on the feed side of the membrane. At sufficiently high pressures, gelation of the macromolecules can occur, resulting in the formation of a thin gel layer on the surface; this can act as a secondary membrane. Increasing the feed stream circulation rate will generally reduce the thickness of the gel layer and increase the flux. Operation within the turbulent flow regime may significantly enhance permeation by reducing the thickness of both the gel and fouling layers, by transferring solids from the membrane surface back into the bulk stream. As with microfiltration, factors of chemical compatibility of materials with the solution will need to be addressed.

8.8 References

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