CHAPTER II

THEORY

This chapter reviews general consideration and theory of Reverse Osmosis and Ultrafiltration membrane and system. Although equations in this chapter may not be directly used in subsequent part of the thesis, they are important in conveying general understanding of the processes involved.

2.1 Reverse Osmosis

The feasibility of the reverse osmosis process was demonstrated by Reid and Breton in 1956 with the finding that the passage of saline water over a supported dense film of cellulose acetate at elevated pressure resulted in the permeation of water with a salt rejection of 95% or greater. The water throughput rate or flux was, however, very low, less than 4.07 $l/m^2.d$ of membrane surface area. In 1960, Loeb and Sourirajan discovered how to prepare an asymmetric or skinned cellulose acetate membrane which enabled comparable salt rejection with an improvement in the flux by about two orders of magnitude, i.e., fluxes of 407.43 l/m^2d or greater at comparable pressures. This finding resulted in a surge of activity aimed at the development of practical systems for desalting brackish and seawater. In 1964, Havens Industry announced the commercialization of a tublar system utilizing a resin-starved fiberglass support tube for the cellulose acetate membrane. Thus, in a period of only about 10 years from the beginning of the work by Professor Reid at the University of Florida, the reverse osmosis process had become a commerival reality.

Significant improvements in this process have been made, and it is now considered to be a vialbe and economical desalination process for many brackish waters. All current commercial reverse osmosis systems utilize cellulose acetate as the membrane material, in sheet, tube or hollow fiber form, except for Du Pont's B-9 Permasep Permeator which utilizes aromatic polyamide hollow fibers. The reverse osmosis process is finding increasing application to various water problems, such as its use in conjuction with ion exchange for the production of high purity water for the electronic industry. Its use for waste water renovation is problematical in certain cases, but with certain improvements it should also find use in this large and important application.

2.2.1 Membrane types

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There are, at present, three kinds of RO membranes available, viz.,

(1) anisotropic or "skinned" cellulose acetate membranes, in sheet, tube, or hollow fiber form,

(2) ion-exchange or polyelectrolyte membranes which are also available in anisotropic form, and

(3) most recently, anisotropic "aromatic polyamide" hollow fibers.

However, only the first and third kind are commercially utilized at present in reverse osmosis equipment for desalting.

The anisotropic cellulose acetate membranes whose acetyl content and molecular weight can each be varied) consist of a relatively nonporous, dense surface layer or skin, approximately 1,5oo to 2,500 Å thick on top of a highly porous (55% void space) substructure which comprises the bulk of the membrane. During reverse osmosis operation, the membrane is employed such that the dense layer or skin faces the feed solution. Desalination occurs at the dense surface layer whose "pores" have been estimated to be less than 8 Å in diameter.

The most common tubular design employs a tube, both as a support for the membrane and as a pressure vessel. Tubes ¼ in. to 2 in. in diameter have been used, with the greatest success having been obtained with ½ in. to 1 in. diameter tubes. In this design, the membrane is inside the support tube where the saline feed passes under pressure. Four types of tubular supports have been employed to date :

(1) rigid porous fiberglass tubes (filament wound or braided),
(2) perforated metal tubes (aluminum, copper-nickel, or stainless steel),
(3) nonporous tubes containing a grooved liner, and
(4) a flexible braided polyester tube.

In the first three cases, the membrane is reinforced with an appropriate backing material or liner to

(1) protect it from damage against the pores, perforations or grooves in the support and
(2) facilitate lateral transport of the permeate from the membrane to these product water channels.

Key features of such systems are

(1) ability to accomodate high flux membranes without a large pressure drop (and hence long tubes can be employed),

(2) ease of cleaning in situ,

(3) possibility of replacing the membrane or the membrane/backing material, with continued reuse of the support tube,

The water content of the skin is estimated to be about 13%, but the water here is evidently in such a form that it neither dissolves nor effectively transports the already hydrated sodium and chloride ions. In a more "open" or porous cellulose acetate membrane, the amount of "unbound" water increases, with a corresponding increase in salt permeation.

Cellulose acetate membranes of different desalination characteristics may be prepared by annealing the membrane (after gelation) at various temperatures; the higher the temperature (up) to about 90°C), the tighter or more semipermeable is the membrane. Thus, for brackish water applications one may employ a relatively open or less "selective" membrane (having a higher flux) compared to that required for the desalination of seawater. A basic problem associated with these membranes (aside from the general problem of fouling) is their tendency to undergo compaction, resulting in an irreversible loss of flux with time. Compaction is more serious for the more open cellulose acetate membranes and increases for all membranes with increasing pressure, particularly above 800 psi.

The aromatic polyamide hollow fibers are a relatively recent development of Du Pont and represent a major advance over the previous nylon type fibers of the "B-5 Permasep Permeator." The new fibers are anisotropic in structure, as mentioned above, with the skin on the external surface of the fiber. These fibers are incorporated in an improved module referred to as the "B-9 Permasep Permeator." Key features of the new system are

(1) an appreciably improved sodium chloride rejection,
(2) over an order of magnitude improvement in flux,
(3) increased lifetime, and
(4) reduced tendency to concentration polarization and fouling.

2.1.2 Module designs

The reverse osmosis process is basically a modular scale process wherein scale-up beyond a given size is not economically advantageous. Several reverse osmosis module configurations have been developed over the past years. As shown in Table 2.1, there are basically four modular designs, viz., spiral-wound, tubular, "sand-log," and hollow fiber, that are now commercially available.

Historically, the first module design was the plate-and-frame design. In this design, the membranes are mounted on rigid plates stacked one on top of the other, within a pressure vessel, with the plates being porous or having grooves for the product water to exit. The spacing between successive plates can vary from less than 10 mil (for laminar flow designs) to greater than 100 mil (for turbulent flow designs). In the latter case, a baffle or porous spacer may be employed between the membranes on each plate to enhance turbulent flow. Key features of this design are

(1) construction,

(2) ability to use rigid membranes,

(3) it can withstand high pressure, and

(4) concentration polarization should, in theory, be readily controlled with this configuration.

The spiral-wound module (Figure 2.1, first developed by General Atomic (now part of Gulf Oil) is so named because the membrane along with the porous plastic support and spacer sheets is wound into a compact spiral unit before placing it into an

Table 2.1

RO Module Designs

Module	Manufacturer
spiral -Wound	Aeroject-Gereral Corporation Eastman Kodak Gulf Oil Company
Tubular	Abcor Aqua Chem Calgon Philco-Ford Corporation
Sand-Log	Westinghouse Electric
Hollow Fiber	Du Pont

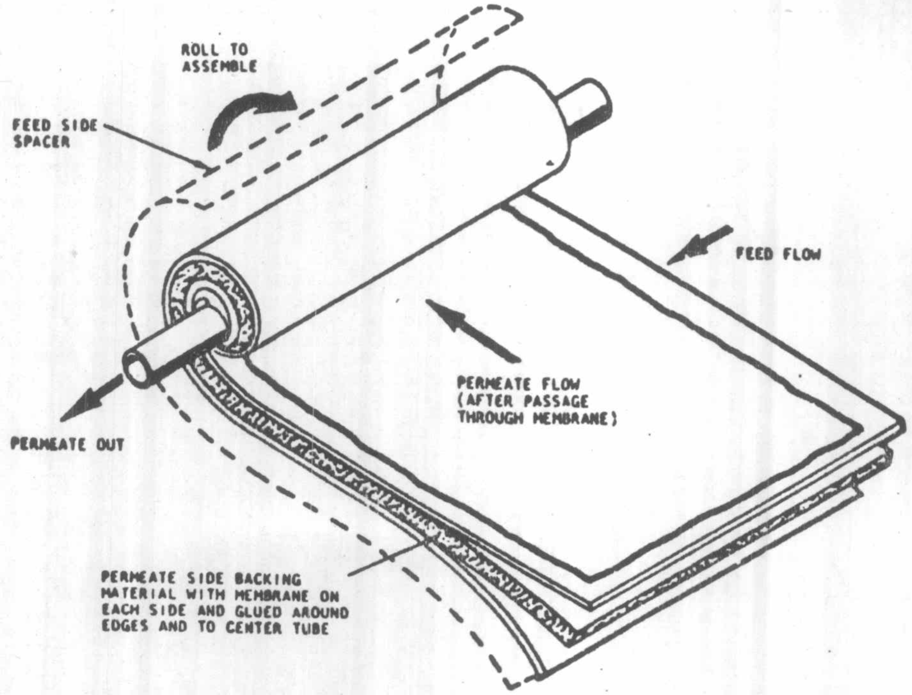


Figure 2.1 Spiral-wound membrane module, partially inrolled.

ordinary pipe which serves as a pressure vessel. The spiral unit consists of a sealed envelope of two membranes containing a product water spacer, 35 to 50 mil thick, separating the two membranes, and a feed-brine spacer between successive envelopes. The envelope is sealed on three edges with the fourth edge open and sealed to a central product water collection tube on which the envelope is wrapped. Specific features of this configuration are

(1) flexible membranes in sheet form can be used in such a way that considerable membrane area can be accommodated in a relatively small volume,

(2) relatively high flux membranes can be employed without a large pressure drop, and

(3) the porous plastic support sheets that are employed are fairly cheap.

(4) ability to handle viscous or concentrated solutions which have a tendency to precipitate solids, and

(5) ability to withstand high pressure, given the proper support tube.

A significant variation of the tubular system is Westing-house's "sand-log" module which consists essentially of a solid core of sand, containing a number of closely spaced ¼ to ½ in. diameter holes, within a metal pressure shell. The membrane is cast directly on the smooth walls of the holes in the sand core, and the latter provides a cheap, effective support for the cast membrane.

The hollow fiber system of Du Pont utilizes a tightly packed bundle of hollow fibers, 1 to 10 mil O.D., 0.2 to 2 mil wall thickness,

Table 2.2

Membrane Configuration, Packing Density, and Flux Density

Module	PD (ft^2/ft^3)	Flux[a] (g/f^2d)	Flux Density (g/f^3d)
Plate and frame	100	20	2000
Tubular (½" O.D.)	67	20	1340
Spiral-Wound	200	20	4000
Hollow fiber	2800	1.8	5000

[a] All at 600 psi except hollow fiber system where pressure is 400 psi

within a high pressure vessel, in a shell-and-tube type of configuration. The hollow fibers serve as the membrane element and as their own support against the pressure of the feed water. The open ends of each fiber loop are potted in a header where the product water from the interior of each fiber exits. An important feature of this system, or the so-called B-9 Permeator, is that the hollow fibers encompass a central porous distributor tube which serves to

(1) filter the feed and
(2) distribute it radially about the fibers.

Specific merits of this system are

(1) it provides a high packing density of membrane surface area per unit volume of module,
(2) the hollow fiber serves as its own support, and
(3) it is lightweight.

It is apparent that there are some advantages and disadvantages for each design. In some cases, this will depend upon the available line pressures, brine disposal requirements, or other more or less fixed parameters. A comparison of the packing density, flux, and flux density exhibited by each (excluding the sand-log system), is shown in Table 2.2. It should be noted that although the flux density is sort of an indicator of the economy of the system, other features, such as cost of assembly, ease of cleaning, membrane lifetime, ability to be regenerated, and scale-up potential, should also be considered in comparing different designs.

2.1.3 Solute and solvent transport relationships

(1) Solvent Transport

Michaels et al. examined the kinetics of salt and water flow across cellulose acetate membranes. Their experiments indicated that water transport across the membrane occurred almost entirely by diffusion through the polymer matrix. This diffusion can be described by the phenomenological expression :

$$J_W = \frac{(\Delta P - \Delta \pi)}{R} \qquad \text{..................(2.1)}$$

where J_W is the transmembrane water flux. R a characteristic resistances of the membrane system to solvent transport. ΔP the hydrostatic pressure difference across the membrane, and $\Delta \pi$ the difference between the effective osmotic pressure of the solutions on the two sides of the membrane.

This expression has been verified for water transport through a membrane from a variety of aqueous ionic and organic solutions by Sourirajan .

When no solute is present, $\Delta \pi = 0$, and the pure water permeability, J_{PWP}, is given by :

$$J_{PWP} = \frac{\Delta P}{R} \qquad \text{................(2.2)}$$

The characteristic membrane resistance, R, can thus be viewed as a measure of the resistance of the membrane to the flow of pure water alone.

Sherwood et al. have investigated an expression for solvent transport which includes a term for viscous flow through large capillaries in the membrane. Their expression was the following :

$$M_w = A_1 (\Delta P - \Delta \pi) + A_2 M_w C_w P_p \quad \ldots\ldots\ldots\ldots\ldots (2.3)$$

where A_1 is a solvent transport parameter , A_2 is the pore membrane coefficient, M_w the molecular weight of the solvent and C_w the concentration of the solvent at the upstream membrane surface. Their results indicated, however, that the pore flow mechanism for solvent transport could in most cases be neglected. Consequently Equation 2.1 will be used in this work to describe solvent flow through the membrane.

Equation 2.1 suggests that the solvent permeability of a membrane is limited primarily by the problems involved in fabricating a membrane with a suitably low characteristic resistance, R. This limitation is almost certainly true for solutions which retain newtonian flow characteristics at all concentrations encountered during membrane processing. In Section 2.2 it is shown that the solute concentration at the membrane surface is higher than in the bulk stream. This existence of a higher concentration of solute at the membrane surface is known as concentration polarization. Many organic substances and especially proteins may show considerable non-newtonian behavior in aqueous solutions. The concentrated boundary layer formed at the membrane surface in these cases may exhibit unusual rheological properties. In addition to non-newtonian effects there may be electro-static interactions between the solvent and solute compoments in the boundary layer. These interactions could further alter its rheological properties. In the concentration and fractionation of organic solutes and foodstuffs, one must therefore examine not only the resistance of the membrane itself to solvent and microsolute transport, but also the resistance of the concentrated boundary layer at the membrane surface. It was shown in the prior section that, in the case of ultrafiltration, the rate of solvent and microsolute transport is governed not by the membrane but by this boundary layer. The operation is then said to be boundary-layer controlled.

(2) Solute transport

In order to understand solute transport through the membrane one must consider both the mechanism of rejection of the solute at the membrane, and the mechanism of transport of the non-rejected species through both the boundary layer and the membrane itself.

In reverse osmosis where even monovalent ions are rejected by the membrane, it seems that spatial criteria alone will not suffice to explain the rejection mechanism. Sourirajan has postulated a preferential sorption-capillary flow mechanism based on the fact that one or more of the solvent and solute species may be preferentially sorbed on the membrane surface. For a reverse osmosis membrane this would require that the water (or solvent) species by preferentially small, only the water will pass through into the pore.

The preferential sorption-capillary flow mechanism of ionic rejection is complemented by Glueckauf's analysis which presents an explanation for the physicochemical criterias which govern the preferential sorption at the membrane-solution interface. Glueckauf postulated that the electrostatic free energy of a single ion in a pore filled with water and surrounded by a membrane of low dielectric constant (i.e., the polymer matrix), is much larger than that of a single ion in bulk solution. The equilibrium concentration of ions in the mouths of the pores is therefore much lower than in the adjacent solution. A single ion entering a pore experiences an electrostatic force which ensures that it is more likely to jump back out than to penetrate further in. This force would not exist if two ions of opposite charge simultaneously entered a pore. This occurrance is unlikely in tight reverse osmosis membranes where the pores will have a size which is smaller than the ionic separation (approximately ten Angstroms for up to 5% sodium chloride solutions).

No single mechanism can be postulated to describe solute flow through the membrane. In some cases, Michaels et al. showed that for reverse osmosis it may be necessary to consider the three parallel mechanisms which are listed below :

i) Sorption and activated diffusion of solute within the polymer matrix, governed solely by the solute concentration gradient across the membrane.

ii) Pressure-biased activated diffusion of solute in near molecular sized pores in the membrane, governed by the hydraulic gradient and the solute concentration gradient.

iii) Hydrodynamic flow of solution through the larger pores.

Later work of Sherwood et al. suggested that in most cases the second and probably the third mechanism can be neglected for reverse osmosis. Sourirajan and Kimura showed that membrane behavior during the concentration of a variety of ionic species from aqueous solutions by reverse osmosis can be predicated by considering only the first mechanism.

In ultrafiltration, where one must explain the mechanism of the transport of a significant fraction of the microsolute species through the membrane, rejection appears to be primarily on the basis of pore size alone. Smaller solute species and solvent can pass through the membrane readily. The passage of microsolutes and solvent from the bulk fluid through the membrane can, however, be hindered by intermolecular interactions in the boundary layer. It is probable that during the transport of microsolutes through the membrane all three of the mechanisms of Michaels et al. will occur. However, there has been no work to substantiate this claim since in most ultrafiltration problems the transmembrane fluxes of microsolute transfer through the boundary layer.

In considerations of solute transport through the membrane, it is convenient to define the percent rejection of species A at the membrane, R_A, by :

$$R_A = \left(\frac{C_1 - C_3}{C_1} \right) 100 \qquad \ldots\ldots\ldots\ldots\ldots (2.4)$$

where C_1 is the concentration of the feed over a given membrane surface area and C_3 that of the permeate from the same area.

In addition to consideration of the problem of solute transport through the membrane one must also consider a mechanism for solute transport to the membrane. During the process of membrane separations one or more of the solute species is completely rejected at the membrane. Solvent and microsolute species which pass through the membrane are supplied to the membrane boundary by bulk flow of feed solution normal to the membrane. The rejected solutes will be carried along in this convective flow. If, however, steady state operation is to be maintained, with all or part of the solute species being rejected at the membrane surface, the excess of the rejected which builds up there must diffuse back into the bulk feed stream. Thus a gradient in the concentration of the rejected species is established in the fluid near the membrane surface such that the net diffusive flux of the rejected species away from the membrane is equal to the convective flux of that material to the wall. The existence of this concentration profile is referred to as concentration polarization. The polarization factor at any point along the membrame is defined as the ratio of the solute concentration at that point to the solute concentration in the bulk feed stream.

Concentration polarization is extremely important because this increased concentration at the membrane boundary may have a number of adverse effects on mass transfer rates and therefore on the economics of membrane separation porcesses. In reverse osmosis, concentration polarization can markedly increase the apparent osmotic pressure of the feed. From Equation 2.2 it can be seen that this increase will increase the operating pressure required to produce a given transmembrane flux. Higher operating pressures will necessarily mean higher pumping costs. In the ultrafiltration of protein and other high molecular weight-solute solutions, concentration polarization may cause the viscosity of the fluid adjacent to the membrane to increase, thereby causing non-newtonian effects or intermoleclular interactions of such magnitude that mass transport from the bulk feed stream to the low pressure side of the membrane may actually be controlled by the rate of diffusion of solvent and microsolute species through the macrosolute boundary layer. Concentration polarization also increases the possiblility of precipitation of marginally soluble constituents in the feed, such as calcium sulfate in brackish water. Such a precipitate can clog the membrane and markedly decrease solvent permeation rates.

2.1.4 Membrane fouling, deterioration , pretreatment

All membrane system undergo fouling and loss of flux with time even with the best pretreatment; i.e., that which is reasonably economical. In addition to the loss of flux, salt rejection may also fall off as a result of chemical or physical deterioration of the membrane. The latter may or may not be associated with the fouling problem.

In examining the overall problem, it is clear that the most important parameters here are

(1) the composition of the feed and

(2) the susceptibility of the membrane and/or module design to fouling and deterioration.

These, in turn, determine the pretreatment and membrane cleaning requirements so that overall capital and/or operating costs are minimized.

In reference to the feed water type, the problems of membrane fouling and deterioration for current systems increase, in general, with the fineness of the particulate matter (such as silica, clays, and organic matter), the hardness of the water, the amount of metallic corrosion products, the concentration of dissolved organics, the presence of bacteria and other microorganisms, and with the concentration of oxidizing disinfectants, such as chlorine. In reference to the membrane type and module design, it is also apparent that certain membranes (in terms of composition as well as "porosity") and module designs will foul and/or deteriorate more readily than others. Thus, the problems of membrane fouling and deterioration are such that they have some features which are specific and others which are common for any given membrane system or feed.

Aside from basic or "primary" pretreatment methods, such as precipitation, coagulation (by physical or chemical methods), settling, filtration through sand, diatomaceous earth, etc., specific approaches that have been investigated include :

(1) chlorination to reduce the bacterial and microorganism content of certain feeds (including seawater) to prevent attack of the membrane,

(2) filtration through carbon to remove organics (such as in secondary sewage effluents) and/or chlorine (in

municipal waters),

(3) addition of sodium hexametaphosphate or other complexing agents for calcium or magnesium ions to prevent precipitation during reverse osmosis,

(4) pH adjustment to prevent precipitation of certain components from the feed and/or to minimize hydrolytic breakdown of the membrane,

(5) addition of activated carbon and Diatomite to form a removable protective "coating" (which also serves as an absorbent) on a cellulose acetate membrane for use in reverse osmosis treatment of primary sewage

(6) use of a surfactant type feed additive, in the ppm range, to form a quasiliquid membrane on the surface of the cellulose acetate membrane, which serves to enhance salt rejection and possibly to protect the surface of the membrane,

(7) use of negatively charged membranes, such as polyacrylic acid (or partially oxidized CA, which has some carboxylic acid groups) to enhance (in theory)rejection of negatively charged colloids (such as the humic acids),

(8) use of oxalic acid, citric acis, EDTA, or other chelating agents to remove metal-containing deposits (such as iron oxide) from the membrane,

(9) use of enzymatic detergents to clean the membrane from organics, and

(10) use of mechanical cleaning techniques, such as blowing a slightly oversized foam ball through the tubular system.

Mechanistically, membrane fouling can occur at the surface of the membrane, within the membrane, or both. In the former case, this can be due to simple filtration of particulate matter present in the feed or introduced from the system (such as corrosion products from the pumps) or precipitation of various solutes due to concentration of the bulk feed during RO. The particulate matter may contain inorganics, such as clay, silica, iron oxide, and other metal oxides,calcium carbonate or sulfate, and organics, such as humic acids, polysaccharides, proteinaceous matter, and microorganaisms. Precipitation of components from the feed depends, of course, primarily upon the component in question and its solubility. In general, it appears that the use of higher pressures tends to compact the deposit more and results in more serious or permanent fouling. However, even this, as well as the various other factors affecting the tenacity of the deposit (formed during reverse osmosis), its form, and exactly how it should affect the membrane's transport properties are not very clear.

The case of internal membrane fouling and/or plugging (and exactly how this should change the membrane's properties) is also not clear. In this case, the membrane's tightness and the specific solute, in question (including its solubility in the membrane), are probably key variables. In reference to the tightness of the membrane, it is generally found that the more "open," higher flux membranes tend to foul more rapidly. The observed flux decline may be due to simple "plugging" of pores or to specific solute-membrane interactions from the surface throughout the thickness of the membrane.

It would appear, therefore, that the use of tighter membranes in conjunction with lower pressures should lead to reduced fouling, with the deposits being more readily removed. An alternative approach is to utilize membranes with higher hydraulic permeability at lower pressures, with more frequent cleaning or backflushing to reduce the accumulation of deposits on and within the membrane.

2.2 Ultrafiltration

Ultrafiltration uses a membrane as a separation barrier. Operating pressure of only 1 to 10 bar (15 to 150 lb/sq. in.) are required to obtain acceptable flows of liquid through the open structure of the membrane. The distinction between Reverse Osmosis and Ultrafiltration is not always clear cut and indeed it is not possible to make a range of membranes with properties varying continuously from the tightest reverse osmosis membrane to the most open ultrafiltration membrane, the point of change from one process to the other is not distinct.

2.2.1 Definition

Ultrafiltration (UF) is a pressure-driven, liquid phase membrane separation process based on the ability of a micro-porous barrier to allow preferential passage of solvent (usually water) and small solute species, and to retain large solute species.

2.2.2 Typical characteristics

The characteristics which are typeical of U.F. are;

(i) solute passing through the membrane are salts and low M.W. ($<$ 500 to 1,000) organics;

(ii) solutes wholly or partially retained are macromolecular (M.W. from 10^3 to 2×10^6)

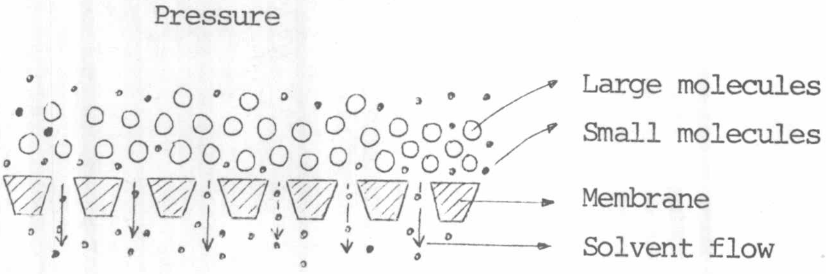


Figure 2.2 Schematic of molecular fractionation by UF membranes

(iii) transmembrane pressures applied are in the range 100 to 700 kPa (1 to 7 bar, or 15 to 100 psi); osmotic effects are usually small;

(IV) solvent fluxes are in the range 10 to 200 l/m^2hr.

2.2.3 UF membrane

(1) General features

UF membranes are usually made from hydrophillic polymers such as cellulose acetate, polysulphone, ect. They are usually formed as a microporous polymer film 100 to 200 μm thick. They are also anisotropic, with a "skin layer" facing the pressurised feed. The tight "skin layer" which is assumed to provide the separation interface, is supported by a more open porous sub-structure (Figure 2.3)

Three points need to be understood about the "skin layer":

(i) this layer is not really an interface - it has a depth of 0.2 to 1.0 μm, and for a typical pore of

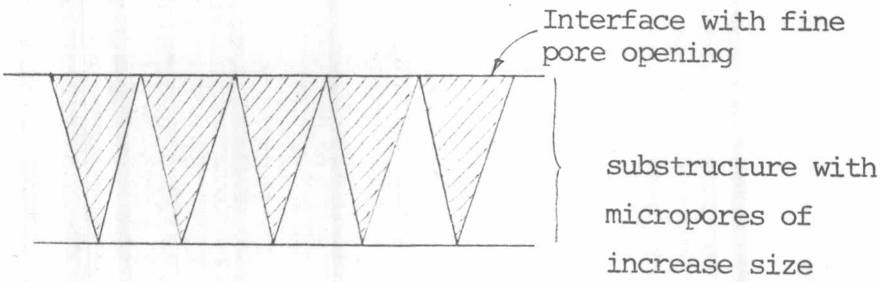


Figure 2.3 Idealised anisotropic UF membrane

diameter 100 A the aspect ratio (length/diameter) may be 100 : 1.

(ii) electron microscopy (e.m.) reveals that the free area of the surface of a typical membrane (combined area of pore openings/membrane area) may be less than 1%.

(iii) e.m. also reveals that there is a distribution of pore diameters at the membrane surface (see Figure 2.4)

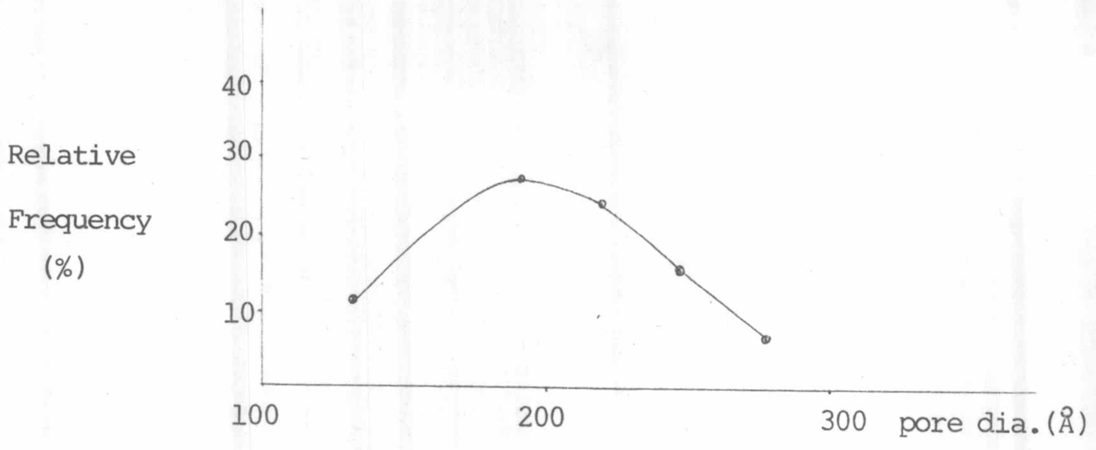


Figure 2.4 Pore diameter VS. Relative Frequency for Amicon XM-100

(2) Transport through UF membranes

(a) Solvent (water) passes through the microporous structure of the membrane by Poiseuille flow as a result of the structure of the imposed transmembrane pressure gradient.

Solvent transport is expressed as a flux, i.e.
Solvent flux, J_1 = vol. solvent/(membrane area.time)
Typical units are l/m^{2}hr, (US) gals/ft^2.day(or GFD).
(note 1 l/m^2.hr = 0.6 GFD).

(b) Solute species pass through the membrane due to both convective flow and diffusion, if the species are

(i) sufficiently small to pass into and through a pore, and
(ii) if they do not interact significantly with the membrane material or other solutes.

In U.F. the convective flow of solute as it is carried by the solvent is usually predominant, and diffusion is normally negleted.

Interest usually centres on solute rejection, which is expressed as,

Solute rejection, $\sigma = 1 - (C_p/C_b)$ ....(2.5)

where C_b is the solute in the bulk feed, and C_p is the solute in the permeate. For a given UF membrane, with its distribution of pore sizes, there will be a relationship between rejection and solute molecular wt. (MW) or size, as shown in Figure 2.5

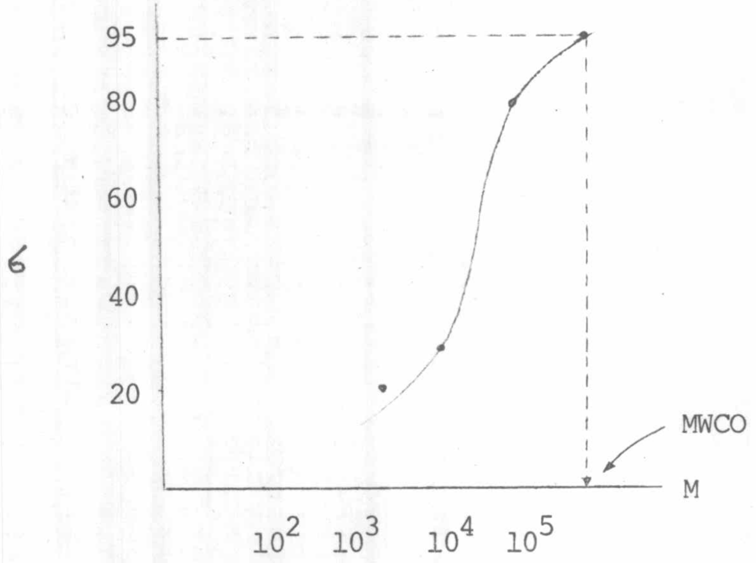


Figure 2.5 Relationship between rejection (σ) and MW (M)

The nominal molecular wt. cut-off (MWCO), of a UF membrane is typically the M.W. of a solute which has $\sigma = 0.95$. However, the MWCO should only be used as a rough guide to membrane selection since it is influenced by operating conditions such as cross flow velocity, pressure, etc. and particularly by the interaction of other solutes in a multisolute system.

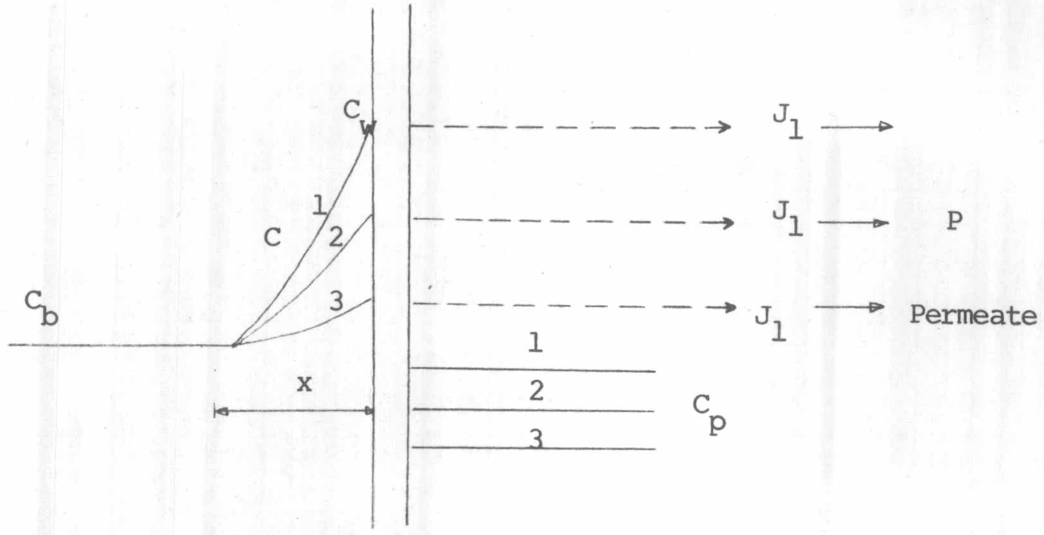
2.2.4 Concentration polarisation and UF theory

(1) Concentration polarisation (C.P.)

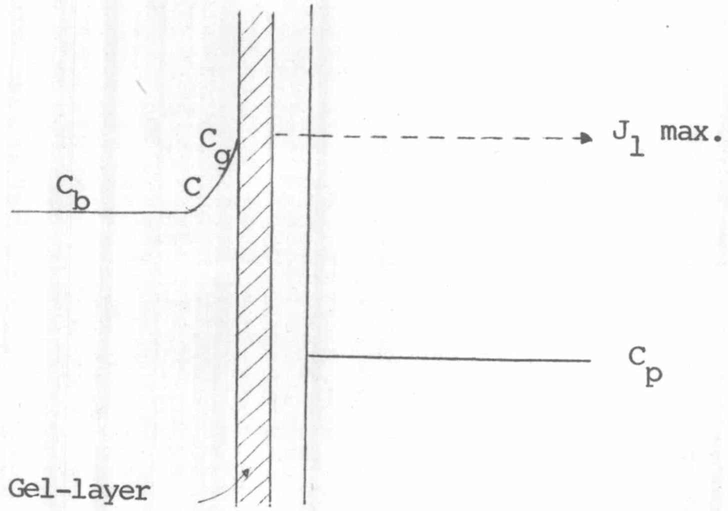
C.P. in UF, and other membrane processes, is an inevitable consequence of the rejection of species by the membrane. These species tend to accumulate and concentrate at the membrane surface, and would continue to do so except for the back-transport to the bulk solution induced by molecular idffusion and eddy diffusion due to cross-flow. At steady state, the net convective transport of solute towards the membrane will be matched by the back-transport from the membrane, and a concentration gradient as depicted in Figure 2.6 will be set up.

For the solutes rejected in UF, C_w can be more than 10 x C_b, and under these circumstances C_w can easily reach a "limiting" concentration where the solute precipitates (or forms a gel, cake or slime layer). This gel provides and added resistance to solvent flow. Attempts to increase flux by increasing the pressure drop only serve to deposit a thicker gel, so that the "steady state" flux fails to increase; it is at its maximum value for the given conditions. Figure 2.7 depicts this situation which is known as Gel Polarised region.

Most practical applications of UF aim to maximise the



<u>Figure 2.6</u> Pre-gel polarisation



<u>Figure 2.7</u> Gel- polarisation

flux and consequently gel polarized operation is to be expected. Note that once a gel layer forms the barrier effecting separation is now a composite of two "membranes" in series, the original UF membrane and the dynamic secondary (gel) membrane. This complicates the analysis of UF performance, as is discussed later.

(2) UF theory

(a) Solvent flux may be expressed in terms of the applied pressure and the resistances,

in pre-gel region, $J_1 = \Delta P/(R_m + R_b)$ ....(2.6)

in gel-polarised region,

$$J_1 = \Delta P/(R_m + R_b + R_g)$$

$$\approx \Delta P/(R_m + R_g) \quad \text{.................(2.7)}$$

To explain the invariance of J_1 with ΔP in the gel-polarised region , R_g must be a function of ΔP.

Note that concentration polarisation introduces resistances R_b and R_g, and thus reduces flux. Indeed R_g may be 10 to 20 x R_m and operational flux will be much less than the membrane pure water flux.

(b) Solute flux has a convective and diffusive component,

$$J_2 = \alpha C_w J_1 - D_m (dC_m/dx) \quad \text{.............(2.8)}$$

D_m = convective diffusive

where α = the fraction of solvent passing through pores capable of allowing solute passage (recall Figure 2.4 for the distribution of pore diameters).

In the pre-gel region, the following approximation can be made.

α = 1 - fraction of rejection solute

i.e. $\alpha = 1 - \sigma_i$ ....(2.9)

where σ_i is the intrinsic rejection coefficient of the membrane. This can be seen by neglecting the diffusion term in equation (2.8) and nothing $J_2 = J_1 C_p$, so that,

$$\sigma_i = 1 - (C_p/C_w) \qquad \text{.............(2.10)}$$

Comparing equation (2.10) and (2.5) it can be seen that the measured (or apparent) rejection coeffient is,

$$\sigma = 1 - (1 - \sigma_i)(C_w/C_b) \qquad \text{...............(2.11)}$$

Due to concentration polarisation (C_w/C_b) 1, so in the pre-gel region,

measured rejection coeff. = intrinsic rejection coeff...(2.12)

For gel-polarised conditions equation (2.12) may not apply.

(c) The conventional model of concentration polarisation in UF is based on the physical models depicted in Figure 2.6 and makes the following solute balance, at steady state,

$$\left\{\begin{array}{l}\text{Solute to}\\ \text{Membrane}\end{array}\right\} - \left\{\begin{array}{c}\text{Solute through}\\ \text{membrane}\end{array}\right\} = \left\{\begin{array}{c}\text{Solute back-transport}\\ \text{from the membrane}\end{array}\right\} \quad ..(2.13)$$

$$\text{i.e.} \quad J_1C - J_1C_p = DdC/dx \quad ....(2.14)$$

Rearranging and integrating across the concentration gradient gives

$$J_1 = \frac{D}{\Delta X} \ln \left\{ \frac{C_w - C_p}{C_b - C_p} \right\} = k \ln \left\{ \frac{C_w - C_p}{C_b - C_p} \right\} \quad ....(2.15)$$

where k is the mass transfer coefficient for the polarising solute in the boundary layer. Equation (2.16) may be rearranged, using equation (2.6) to give,

$$J_1 = k \ln \left\{ \frac{C_w - C_b(1 - \sigma)}{\sigma C_b} \right\}, \text{ for partial rejection} \quad ......(2.16)$$

or

$$\underline{J_1 = k \ln (C_w/C_b), \text{ for complete rejection}} \quad ....(2.17)$$

Equation (2.17) applies to the pre-gel region. When $C_w = C_g$,

$$\underline{J_1 = k \ln (C_g/C_b), \text{ gel-polarised, total rejection}} \quad .....(2.18)$$

Equation (2.18) is the most commonly used relationship of the C.P. model, and it is discussed in some detail below.

(d) Discussion of the flux relationship, $J_1 = k \ln(C_g/C_b)$

(1) Flux decreases in semilog relationship with solute concentration, and approaches zero as C_b approachs C_g.

(2) Flux may be increased by increasing the value of k, the solute mass transfer coeffient. In general

$$J_1 \propto K \propto \underbrace{\frac{D}{x}(Re)^n \; (Sc)^m \; (x/L)^p}_{\text{available mass transfer correlation.}} \quad \ldots\ldots\ldots\ldots\ldots(2.19)$$

It is most unlikely that equations (2.18) and (2.19) can be used for a prior prediction of J_1, because

(i) the available mass transfer correlations are usually more applicable to lower Schmidt number situations;

(ii) there is uncertainty concerning the choice of solute concentration at which the physical properties should be calculated for Re and Sc;

(iii) there is often uncertainty about the nature of the major polarising solute in a mixed system.

(iv) there is no reliable method of predicting the gel-concentration, C_g.

(v) the model assumes that the properties of the membrane may be ignored in the gel-polarised region; this is discussed in (c).

Inspite of these limitations the relationship provides a great deal of insight into the effect of changes parameters on flux J_1.

Table 2.3 summarises the forms of the mass transfer correlations for use in equation (2.19), for laminar and turbulent flow conditions in stirred vessels, flow channels and tubes.

In particular, the exponents n, for channels and tubes in both laminar and turbulent flow are often greater than indicated and may reach 0.5 for laminar flow and 0.1 or greater for turbulent flow. Greatest discrepancies occur for colloidal species and suspended solids. The exponent p for channel or tube length has been found to be 0.0 under certain circumstances.

To Summarise :

- Flux may be increased by various "fluid-management" techniques.
- In stirred vessels flux increases as stirring speed increases.

TABLE 2.3 Mass transfer correlations for use in equation 2.19 for various hydrodynamic conditions

$$J_1 \propto k \propto (D/X)\ (Re)^n\ (Sc)^m\ (X/L)^p \quad \ldots\ldots\ldots\ldots\ldots (2.19)$$

Regime	Geometry	Characteristic Length (X)	Exponent		
			n	m	p
Laminar*	Stirred Cell	Cell radius (r)	0.55	0.33	0
Turbulent	S.Cell	Cell radius	0.75	0.33	0
Laminar	Channel**	Channel height	0.33	0.33	0.33
	Tube***	Diameter	0.33	0.33	0.33
Turbulent	Channel	Equivalent	0.80	0.33	0
	Tube	Diameter	0.80	0.33	0

Note :* $Re = (\omega r^2/\nu)$; $8000 < (Re) < 32{,}000$

** more often reported as $J_1 \propto (\dot{\gamma}/L)^{0.33}(D)^{0.67}$ ... (2.19a)

where $\dot{\gamma}$ = fluid shear rate

= 6U/channel height .... (2.19b)

*** as above, with $\dot{\gamma}$ = 8U/diameter

- In laminar flow systems flux increases with shear rate and flow velocity decreases with channel height or diameter, and may decrease with channel length.
- In turbulent flow systems flux increases with flow velocity, decreases with channel equivalent diameter and is independent of channel length.
- The effect of changes in physical properties may be estimated from (2.19). For example the general effect of increase in temperature, which increases diffusivity, D, and decreases the kinematic viscosity, ν , can be shown to increase flux .

(3) According to the concentrational model expressed by equation (2.18) flux is independent of membrane properties in gel polarised operation. This implies that membranes with different permeabilities to solvent flux will give the same flux, assuming complete rejection of solute. Equation (2.18) also fails to account for the possiblity of flux decline shown in Fig. 3.11. To allow for this the model can be modified to give,

$$J_1 = x_A \, . \, k \ln (C_g/C_b) \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.20)$$

where, x_A = the fraction of active membrane surface.
Note that x_A will be proportional to the fractional free area (combined area of open pores/membrane area), which means that membranes with more free area will have higher flux, and fouled or plugged membranes will have a lower flux.

2.2.5 System design

(1) Module design

A wide range of UF modules is available. In general modules are designed to provide an appropriate cross flow regime to minimise concentration polarisation, to provide adequate support for the membrane, to provide a large area/volume ratio, to provide a means of permeate collection, to be readily cleaned or sanitized, and to be easily replaced or remembraned.

The following briefly summarises the designs;

(a) Stirred vessels

These are usually small, bench-scale ultrafiltration units which are useful for small batches of process solution or for research studies. Scale-up from stirred cell studies is hazardous, although the data may help in membrane selection. Unfortunately only a small number of the large-scale membranes are available in the sheetform required for the stirred cell. The flux dependency on operating variables may be estimated from the information in Table 2.3.

(b) Laminar flow systems

These modules usually rely on high shear rate, $\dot{\gamma}_w$, to permeate flux. This can be achieved by using small diameters or channel heights. Designs include thin channels, hollow fibres, spiral wound modules, splined rods ect., and these are detailed elsewhere. The advantages claimed for the laminar flow systems are that they provide a large area/unit volume and a more efficient cross-flow technique. However, they have the disadvantage of being readily blocked, and are not suitable for "dirty" applications without pretreatment. Some laminar systems are not easily cleaned.

(c) Turbulent flow systems

These modules are either tubular (12 to 25 mm dia.) or thin channel, and these are detailed elsewhere. They have the advantage of being able to handle "dirty" applications and are usually readily cleanable. One the other hand they do rely on larger volumetric pumping rates than the laminar flow systems.

A comparison of laminar and turbulent systems may be obtained by comparing the ratio of the mass transfer coefficient k to the pressure drop along the channel ΔP_c, which shows,

$$\frac{(k/\Delta P_c)\ \text{turb}}{(k/\Delta P_c)\ \text{lam}} = 2.5\ Re_L^{-0.3}\ (1+R)^{-0.95}(L/d_e)^{0.33} \qquad \text{...........(.2.21)}$$

where Re_L is the Reynolds Number in a laminar channel without reciculation, and R is the recirculation rate necessary per unit for feed rate to make the same channel turbulent.

(2) Plant configuration

UF processes can be operated as either batch or continuous processes.

(a) Batch

This approach is suited to small to moderate quantities of feed solution, and where intermittent operation is either desirable or not difficult.

Figure 2.9 shows two schemes for batch concentration. Scheme I concentrates by recirculation through the holding tank, whereas Scheme II recirculations in the UF loop and the tank feeds the loop to replenish permeate. As can be seen from Figure 2.10 Scheme I is intrinsically more efficient since it is always operating at the lowest possible concentration at the ultrafilters. It also requires less membrane area than the equivalent continuous UF system. Howerver it require the greater need of pumping power, and requires longer retentime which may not be suitable for certain materials.

Calculation of batch-time (t) or area requirements A_m, can be made once the relationship $J_1 = f(C_b)$ is known from pilot trials. An approximate solution can be obtained by assuming an average flux over the range of concentations. A precise approach is to apply the relationship,

$$\frac{A_m t}{V_o} = C_{bo} \int_{C_{bf}}^{C_{bo}} \frac{1}{J_1} \, d\left(\frac{1}{C_b}\right) \qquad \text{..............(2.22)}$$

assuming complete rejection.

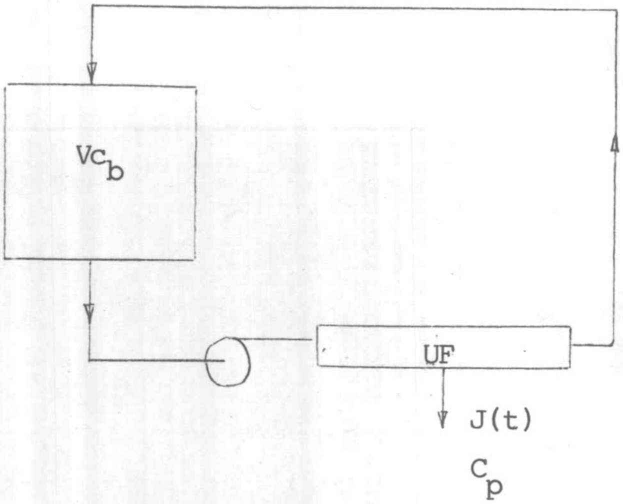


Figure 2.8 Scheme 1

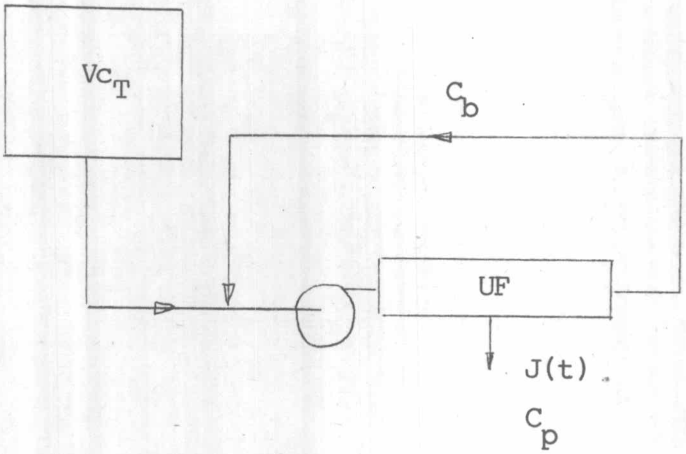


Figure 2.9 Scheme II

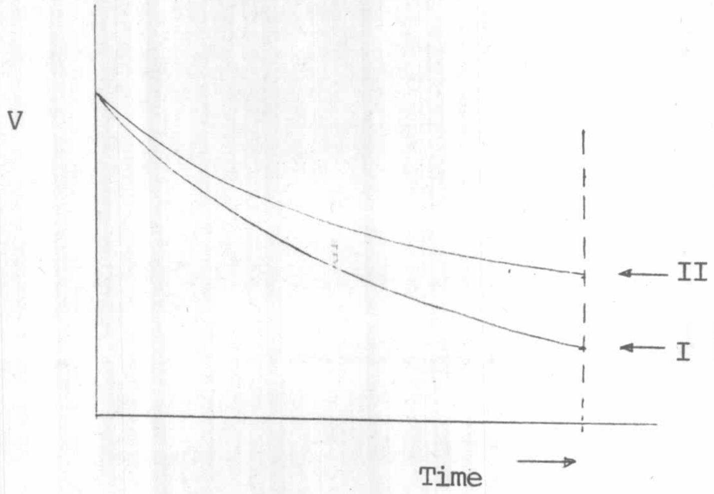


Figure 2.10 Batch volume vs. time

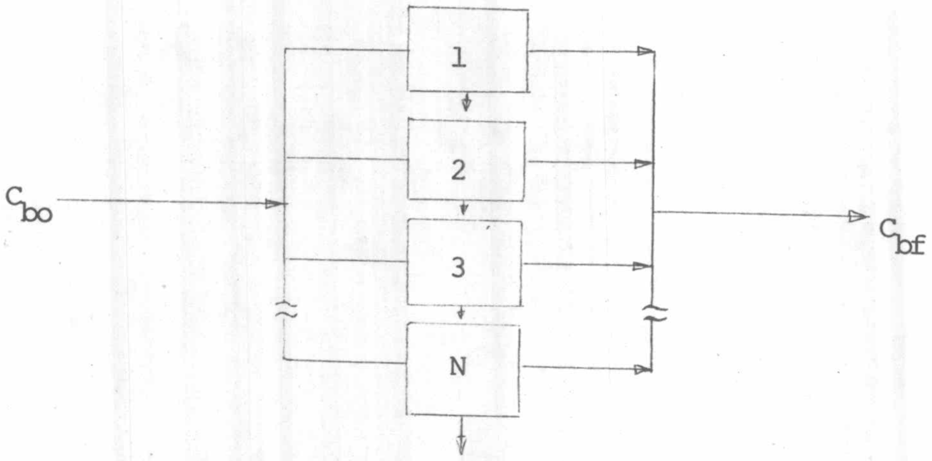


Figure 2.11 Parallel flow-this requires the most membrane area

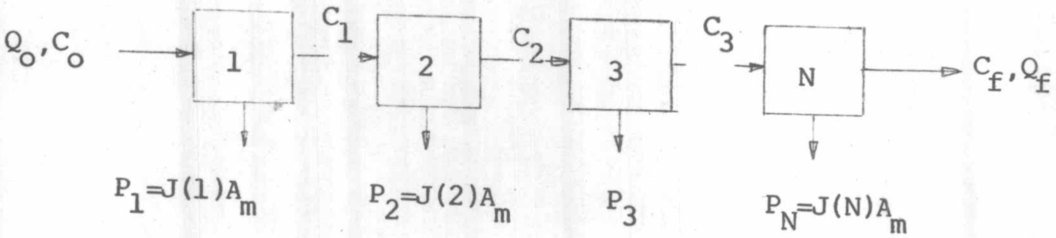


Figure 2.12 Series flow equal sized stages

Where V_o is the initial volume, C_{bo} and C_{bf} are the solute concentrations in the original and final batch. Equation 2.22 can be solved by plotting $(1/J_1)$ VS $(1/C_b)$ and integrating graphically.

(b) Continuous operation

This approach is most suitable for large volume flows and where intermittent operation is not feasible. Due to the modular nature of UF equipment at whole range of arrays is possible, and Figure 2.11 indicates the two extreme cases of parallel flow and series cascade with N equal sized units.

Parallel flow requires the most membrane area since all units will be operating at the highest (product) concentration and will have the lowest flux.

Continuous flow with equal membrane area in each stage is the simplest form of series operation. Tapered cascades with more area at the head end may be more efficient; calculation of the most efficient cascade is a complex optimisation problem.

For the simple cascade shown in Figure 2.12 the number of stages can be calculated once the $J_1 = f(C_b)$ data are known. A series of mass balance are made to determine the concentrations between stages; the calculation can be made from the feed to the product end (forward calculation) or from product back to feed (backward). The forward calculation involves trail and error, but is more accurate since it commences with the known feed condition.

2.2.6 Factors affecting membrane performance and service life

(1) Water flux

The most basic measure of the performance of a membrane is its water flux. This is the rate at which distilled water permeates the membrane under a given transmembrane pressure. A typical water flux for ultrafiltration membrane under a transmembrane pressure of 3-5 bar would be 100-500 l/m^2hr. This will depend on the "tightness" or molecular weight cut-off of the membrane, with low molecular weight cut-off membrane having a low flux.

After a membrane is cleaned, it is usual to check the water flux to see if the original water flux has been largely restored.

A note of caution should, however, be injected about water flux tests. If a new membrane is taken and subjected to expanded water flux testing, its flux may drop appreciably as a result of either hydrolysis of the membrane material or reorientation of the polymer molecules comprising the membrane.

Curve A on Figure 2.13 shows the result of extended water flux testing on an Amicon PM10 membrane at 100 kPa. After 200 minutes the flux has dropped to a fraction of its original value. The original flux is not restored by standard cleaning methods. However, when the membrane is first used with protein solutions and then cleaned, curve B results. Apparently the protein has stablised the membrane structure. Similar results have been observed on commercial ultrafiltration modules, but do not appear to have been widely recognised by membrane manufacturers or users. The implications are clear. Membrane must not be subjected to extended water testing before they have been put into process service.

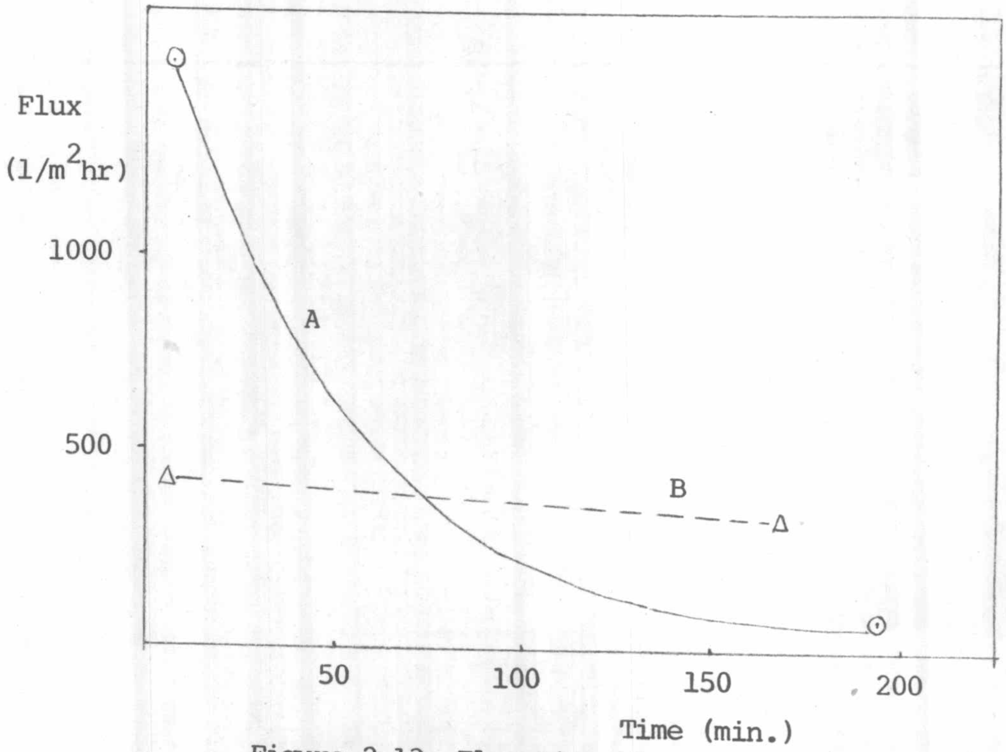


Figure 2.13 Flux-time plot of water

(2) Service life

In service, the flux of a membrane quickly declines from an initial value to a slowly decreasing value as in Figure 2.14.

The reason for the continuing decline is not entirely clear as the gel layer itself is rapidly established (matter of minutes). However, it is likely that the decline is a result of the progressive blockage of membrane pores. This leads to a modification of the membrane area and a decrease in flux according to Equation 2.22 . After a certain period of time, it becomes necessary to clean the membrane to restore its flux. Cleaning is usually done by first washing with water, following by detergent or enzyme solution and lastly by further water.

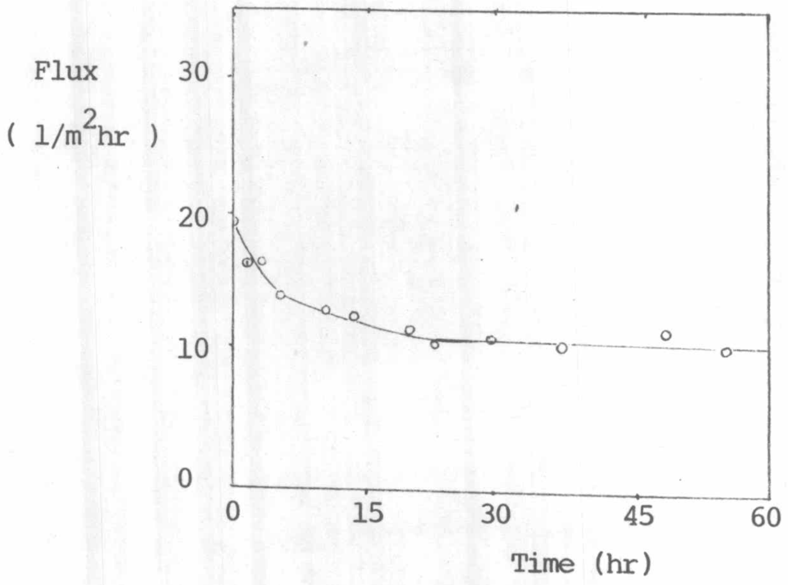


Figure 2.14 Decay of ultrafiltration flux with time

Each membrane manufacturer offers his own prepared cleaning procrdure. The experimenting with different cleaning solutions (e.g. caustic soda, other enzymes) can lean to an optimum cleaning sequence for each type of process stream.

The frequency with which cleaning should be carried out also depends on the destination of the final concentrate product. If it is to be used for human consumption, as in diary whey and starch effluent ultrafiltration, membrane and system need to be sanitised regularly, generally once diary. The steps taken this cleaning and sanitation procedure can largely restore the throughput of the membrane, and average fluxes of 50-80 l/m^2hr ± or whey ultrafiltration can be maintained over a long period.

Ultimately, however, despite the frequency and efficiency of the cleaning procedure, the membrane performance will have declined to such an extent that replacement is necessary. As an example, in diary ultrafiltration plant, the membrane are replaced when the water flux after cleaning has dropped to one-half or one-third of that of a newly commissioned membrane. It is a step ont to be taken lightly as the membranes represent up to 10% of the capital cost of membrane plant. On average it is necessary to replace the membranes once per yerar.

(3) Effect of solids in feed

Provided that particles size of solids present in the feed to an ultrafilter is not such that the particles block channels in the ultrafilter, the presence of such solids can assist the ultrafiltration process. This is illustrated in figure 2.15 where the flux-concentration plot for wheat starch factory effluent shows a marked trend away from a semi-logrithmic plot at high solids concentration. At concentration beyond 2 wt.%, the solids present increase the attainable flux appreciably. In limited experiments where solids are diliberately to the feed stream to an utrafilter and have obtained significant increases in flux. However, this approach presumes that a concentrate contaminated with added solids is equally valuable. Clearly, the choice of solid to be added is thus of importance. For wheat starch factory effluent, for example, a suitable solid is bran or wheat fibre.

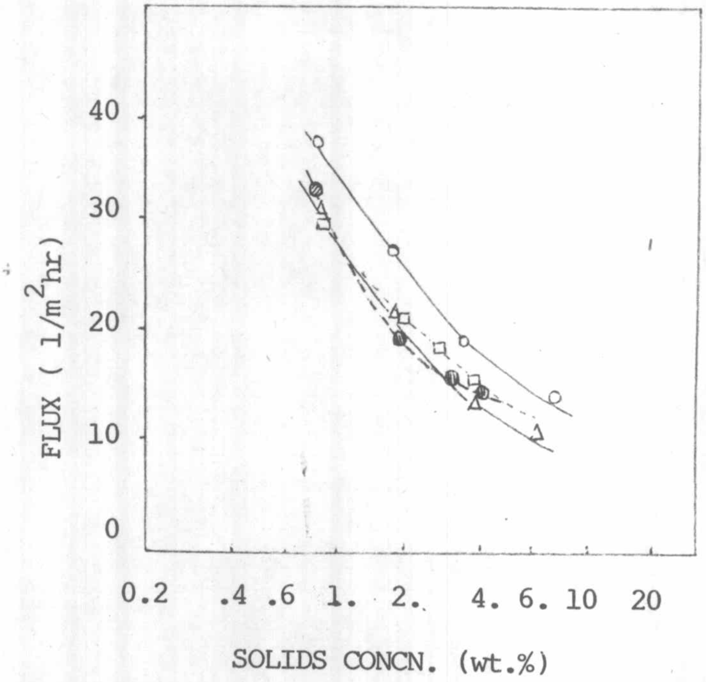


Figure 2.15 Flux-concentration plot for wheat starch

: process side flow rate 230 l/hr
: process side flow rate 12,000 l/hr
: process side flow rate 300 l/hr
: process side flow rate 810 l/hr