

# PROCESSES MEMBANE

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## CHAPTER 1

### INTRODUCTION TO MEMBRANE PROCESSES

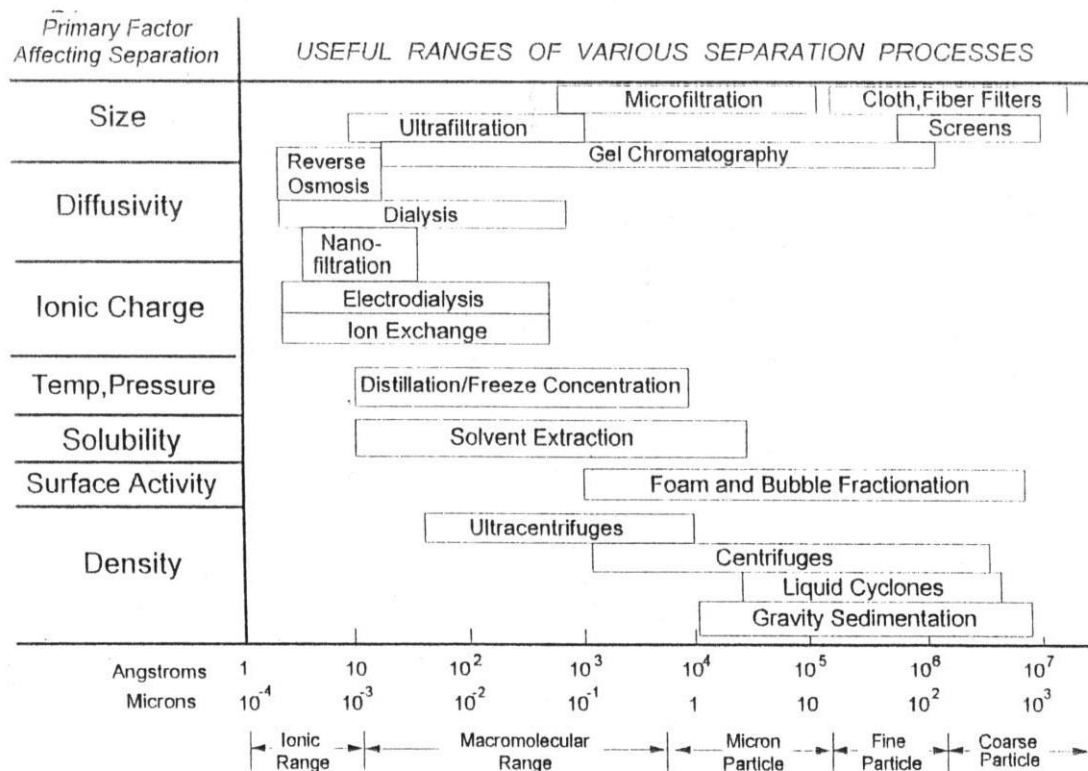
The filtration is defined as the operation of two or more components present in a separation fluid, essentially based on the difference of the size of the components themselves. In Conventional filtration refers to solid particles suspended in a liquid or in a solid. There filtration through membrane extends this application including the separation of solutes dissolved in a liquid stream and those of gas mixtures. The primary role of a membrane is to act as a selective barrier, which can allow the passage of certain components and It considers other components of the mixture. In its broadest sense can be a membrane defined as a discontinuity region which is interposed between two phases. The membrane can be consists of a homogeneous or heterogeneous phase and in particular from one of the following materials or a combination thereof: solid non-porous, microporous or macroporous solids with a fluid (gas or fluid) in the pores, a liquid phase or a gel. The phase membrane interposed between the two other phases controls the exchange of mass between them: this consists in the process or membrane. One of the components of the mixture is transferred preferentially to the other phase, so that the membrane operates selectively on the components of a mixture. A phase is enriched with a component and the other is impoverished. A process or membrane, therefore, allows a selective and controlled transfer of a component from the heart of one phase to that of the phase separated from the membrane. The transfer of each component through a membrane is caused by one or more forces pushing, which can be represented by a chemical potential or an electric potential. The chemical potential gradient can be formed by a concentration gradient or by one of pressure or both. The flow through the membrane of each species per unit of force prompting is proportional to the permeability of species. If the pushing force is made up of a pressure gradient,  $\Delta P$ , or a concentration gradient,  $\Delta c$ , the flow through the membrane the i-th species is given by:

$$\text{Flow of the species i-th} = \frac{\text{species of permeability}}{\text{thickness of the membrane}} (\Delta P \text{ or } \Delta c).$$

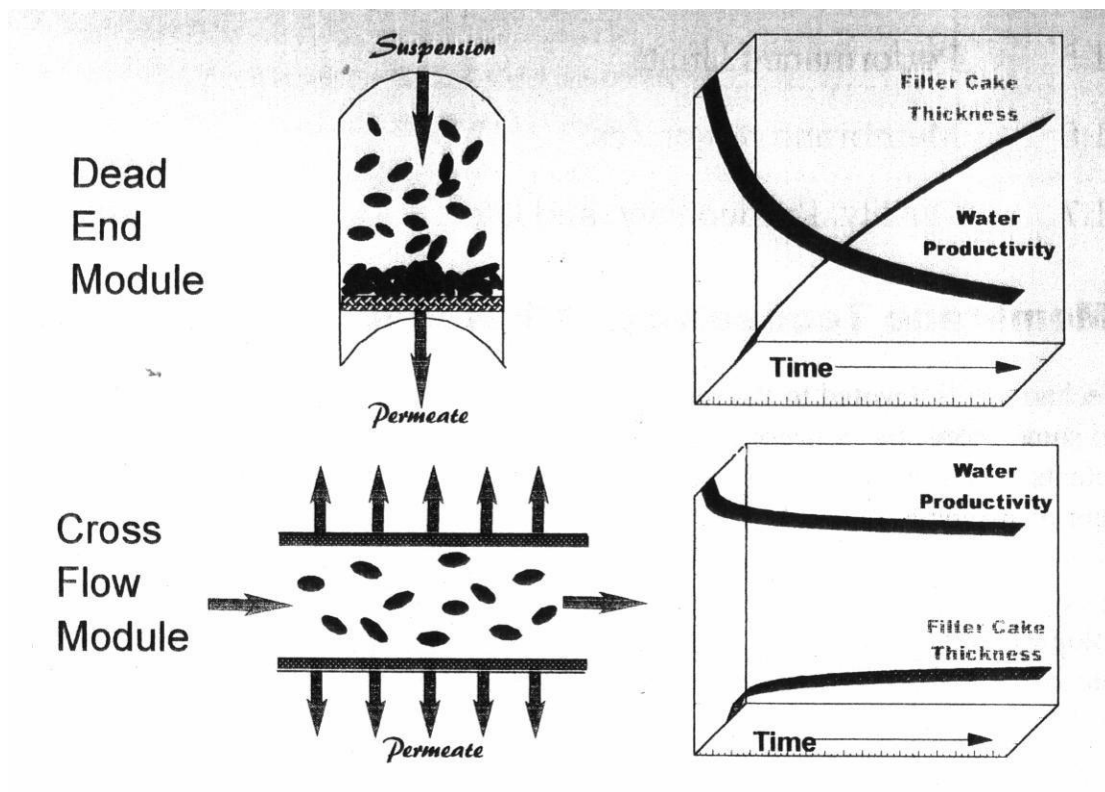
The phase, constituted by components that are not transferred through the membrane, which leaves process is called rejected, while the phase formed from the species that pass through the membrane called permeate. The membranes can physically or chemically modify the components that permeate the same membrane (ion-exchange membranes or bifunctional), can lead

electric current or simply adjust the flow rate of the permeate, so that the membranes can be passive or reactive to the process. Groups in which there are ions and the pores present in a solid phase to give a membrane of the semipermeability properties. In Figure 1.1 shows the characteristics of various membrane processes. Reverse osmosis is the preferential transport of the solvent through a semipermeable membrane from a solution concentrated to a diluted solution that is located on the other side of the membrane, under a gradient pressure. Conversely, the electrodialysis enables to pass preferentially ionic species through a membrane to the ends of which it is applied an electric field. In both cases we can obtain the separation between the water and the salts present in the solution, but through a different principle of separation, that is, through a different technology based on membrane process. A feature that creates distinction between the membrane processes is the direction of the fluid flow. Tangential, it may be tangential with respect to the membrane or in the direction of the surface of membrane. The benefit of the first type of flow that characterizes most of the processes is the fact that the solute or suspension which tends to concentrate / accumulate on the surface of membrane is removed from the fluid stream that runs tangentially to the surface of the membrane. In this manner, the process tends to reach its steady state unlike to what happens in filtration, where the direction of the fluid supplied is perpendicular to the bed, in which case we have a continuous accumulation of suspended solids on the filter bed (see Figure 1.2). Membrane processes most common, those in which the pushing force and pressure are characterized by an increasing range of pressures applied in the order in microfiltration, ultrafiltration, nanofiltration and reverse osmosis. The nature of the membrane which controls component can pass through the membrane and which is arrested by the diaphragm itself (see Figure 1.3). In an ideal reverse osmosis it holds all the components except the solvent (eg water), while the ultrafiltration only retains macromolecules or greater than 10-200 particles angstrom. (0.001 - 0.02 microns). The microfiltration, however, retains particles suspended in the field 0.10 - 5 microns. So you can say that the reverse osmosis is a technique to get water adequate purity, while the ultrafiltration is a technique that can be used to purify a solution separating macromolecules, but at the same time can be seen as a way of concentrating a solution, the rejected, in which they remain such macromolecules. Finally, the Microfiltration is a technique of clarification of a solution by means of the separation of solids suspended. Nanofiltration is a relatively new process based on the use of membranes. They have larger pores than those of reverse osmosis membranes, but not salts to pass many organic compounds such as sugars. In Figure are examples of compounds which can be separated by different processes. The membranes are usually classified on the basis of size

of components to be separated (see Figure 1.4). In the microfiltration (MF), the size is expressed in microns. Ultrafiltration (UF) refers to the "molecular weight cut-off" (MWCO), this arises by the fact that the UF membranes are used to separate proteins, polyethylene glycols, etc. these compounds characterized by their molecular weight. In these terms the UF process concerns the separation of molecules ranging from a molecular weight of 1000 to about 500 daltons. both productivity properties, in terms of flow of permeate, and the degree of separation of the components depend on the kinetics of transfer of different species through the membrane, which in turn time depends on the material and the structure of the membrane. Sometimes these two characteristics are in contrast in the sense that when it is increased transfer speed (speed of permeation) using more permeable membranes. They make the worst performance as relates to the degree of separation. In the gas molecular separations there may be a compensation between permeability and selectivity. An example is the movement between productivity and selectivity that occurs for separating oxygen / nitrogen through polyimide materials (see Figure 1.5).

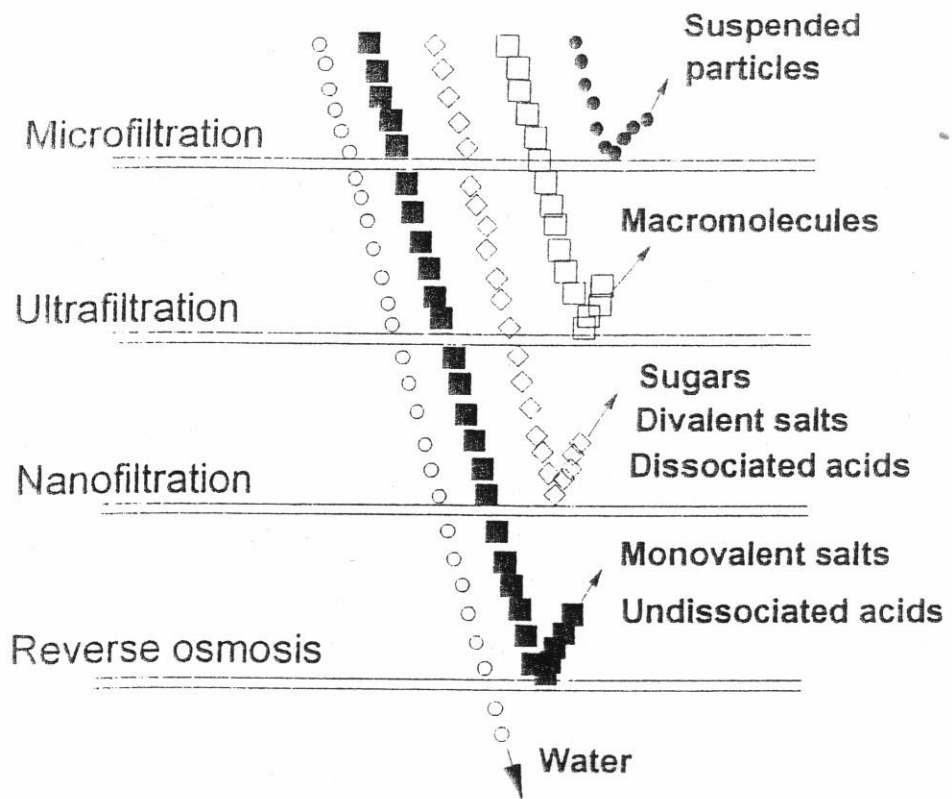


**FIGURE 1.1:** Use of separation processes as a function of the size of the material from to separate.



**FIGURE 1.2:** Schematic illustration of the difference between perpendicular filtration and filtration Tangential.

## Membrane Separations

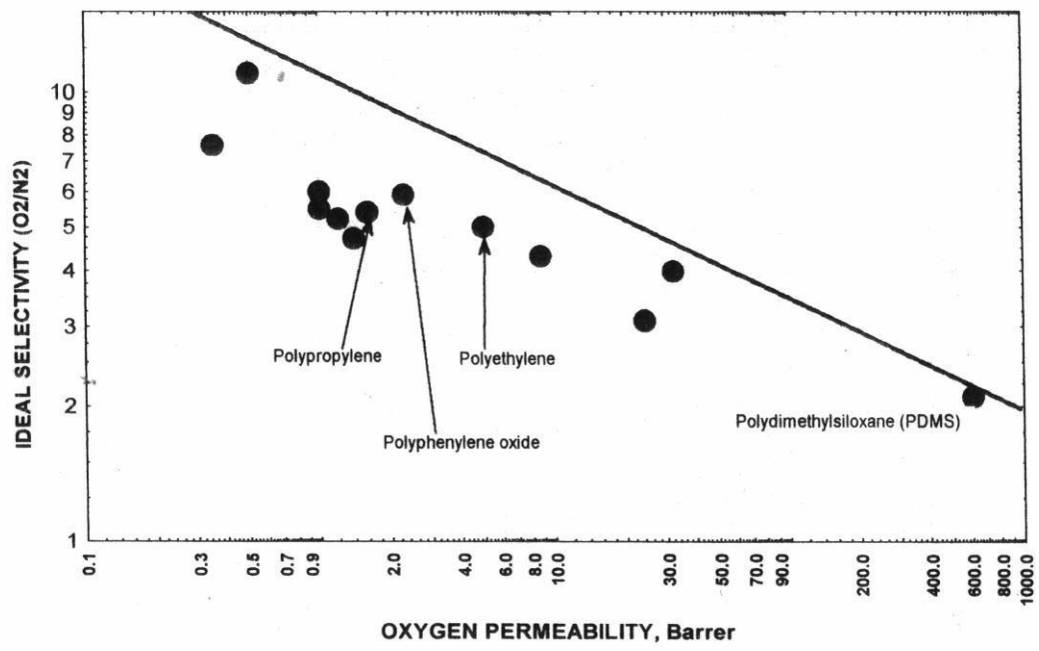


**FIGURE 1.3:** Separation processes in membranes having the pressure as pushing force.

SIZE	MOLECULAR WEIGHT	EXAMPLE	MEMBRANE PROCESS
100 $\mu\text{m}$		Pollen	MICROFILTRATION
10 $\mu\text{m}$		Starch	
		Blood Cells	
1 $\mu\text{m}$		Bacteria	
		Latex emulsion	
1000 Å (100 nm)			ULTRAFILTRATION
100 Å	100,000	Albumin	
	10,000	Pepsin	
10 Å	1000	Vitamin B-12	
		Glucose	NANOFILTRATION
		Water	REVERSE OSMOSIS
1 Å		$\text{Na}^+ \text{Cl}^-$	

**FIGURE 1.4:** Size of the particles can be separated with the membrane processes having the difference pressure as a pushing force.





**FIGURE 1.5:** The relationship between productivity and selectivity in separating  $O_2/N_2$ .

## **CHAPTER 2**

### **THE STRUCTURE OF SEPARATION MEMBRANE**

The membrane is a more or less thin interphase which is interposed between two phases of different characteristics, separating each other. In addition, the membrane selectively reduces the transport of chemical species present in the two phases. The incoming current in the membrane is called feeding, outgoing current from the rejected concentrated or system, while the current that passes through the membrane is called permeate. An ideal membrane should allow the simple passage of the solvent and completely prevent the diffusion therethrough of solutes. In this manner, it is possible to obtain a very dirty concentrated phase of solutes (the concentrate or rejected) and another phase of pure solvent (the permeate). The membrane can be homogeneous or heterogeneous, symmetrical or asymmetrical, solid or liquid, electrostatically neutral or electrostatically charged. The thicknesses of a membrane ranging from hundreds of nanometers to over one centimeter. The mass transport through the membrane can occur in convective flow or diffusion of single molecules. The pushing force of the process is a combination of the pressure, temperature, the concentration gradient and the electrical potential.

#### **microporous membranes**

The microporous membranes have a very simple structure, similar to those of a size filter from fibrous material. The pore size of this membrane ranging from  $<1$  to  $20\text{ nm}$  min. The main mechanism is convective, similar to what is observed during the sieving, determined by the relative size of the pores to that of the particles. The material It constitutes the membrane can be ceramic, metal, metal oxides, graphite or polymer. There structure can be symmetrical or asymmetrical. It does not take special membranes symmetrical as larger particles which enter from the surface would end with the block along the smaller pores of the membrane layer therefore operates with membranes asymmetrical which have a surface layer that prevents the passage of the particles big (skin or skin) and an underlying layer macroporous which also serves as support to the skin membrane. E 'the surface layer which then realizes the selectivity of the membrane or determines the MWCO (molecular weigh cut-off). Depending on the materials that will constitute the matrix of the structure that is intended to achieve, the production methods of the membranes vary greatly. The most common basic process is one called "inversion of the solution." The

process consists in the precipitation by immersion, in separate stages. It dissolves in a polymer a suitable solvent (acetone, dioxane, etc.) and is added to a swelling agent (Swelling) consists of magnesium perchlorate or formamide. When this solution is poured heated on a structure that generates evaporation on the surface of the solvent takes place forming phenomenon (casting). The polymer for that protrudes from the surface evaporation solvent itself and forms the skin of the membrane (skin). Subsequently the solvent continues to evaporate slowly while the blowing agent separates as a distinct phase. The supporting structure with the overlying polymer film is placed in contact with the water that diffuses through the film that has been created by expelling from it the non-solvent, the swelling agent, to create a structure porous (moneycomb) a. By selecting appropriately the solvent and the forming times before of contact with water it is possible to obtain a good asymmetry and control the structure of the membrane.

#### composite membranes

One of the biggest problems with asymmetric membranes (see Figure 2.1) used for the osmosis reverse is the use of the same material to perform different functions: the separation, support, protection. In these cases it became obvious to resort to a membrane composed of different materials that perform different functions. The biggest challenge has been to ensure the permeability or surface dense films that are very thin. The two solutions to the problem of Most commercial success are as follows. Not so much I chose to make the coating of a porous membrane with a layer of plolimetilsilosano (PDMS) highly permeable. The coating eliminating surface defects allows you to make much more selective membrane. A second technology is that Filmtec, marketed by Dow Chemical, it consists in creating a surface layer of polimerice membrane by reacting the two monomers on a support polisulfonico so as to form a polyamide coating. (See Figure 2.2). Other possibilities are offered by the dip coating of the membrane with a polymer with an intrinsic selectivity.

#### ceramic membranes

Ceramic membranes were developed for the nuclear industry, to separate isotopes uranium 235 and 238 through their fluosati compounds. The separation is based on micropores that ranging from 6 to 40 mm. Ceramic membranes are nowadays used industrially particular attention in separation processes with aggressive solutions. They are available in oxides

of zirconia, alumina and titanium oxides. To create asymmetric ceramic membranes are manufactured with a series of superimposed layers. The membranes in nitrogen zirconia offer the greatest porosity and are used in MF, while those of titanium oxide have minor porosity and are used for NF processes.

#### Modules and membranes

The four categories of constructive units, "modules" of membranes (packing of membranes) are:

- plates and dividers
- coiled
- hollow fibers
- tubular

#### Modules and dividers

They are the simplest systems and developed the first (see Figure 2.3). They are simple to assemble, sterilize and replace it with a new membrane, the latter particularly useful thing when the membrane is subject to fouling, on the other hand reassemble the different dishes is not very smoother. Ultimately they are used for small-scale systems such as those pharmaceuticals. In this case the cost of the membrane is minimal compared to the equipment as a whole.

#### Spiral wound Modules

And the most widely used system as the units of this type are easily replaceable in a Membrane plant (Figure 2.4). In addition, the spiral modules have a high area per unit of volume (of the order of thousands of meters squared per meter cubed), with a reduction of volumes required for the housing of the membranes. These modules are used for the separation of gases and liquids (UF, NF, RO). The structure of the membrane can be considered as a series of plastic bags equipped inside of a spacer to allow the passage of the permeate with the active part of the membrane on the outside (see the bottom part of Figure 2.5). The length of each module ranges from 1 mm to 1.5 mm. The diameter and length are expressed in inches, so for example, a membrane with 8/2 in diameter and 40 seconds in length is classified as 8040 while a membrane with 4 seconds of diameter and 40 seconds in length is called

4040. The maximum that can be used is 80 ° C, provided that the materials of all constituent elements so permit. In Figure 2.5 the dimensions of the different parts are indicated one of the elements of the membrane module. The supply channel, which has a width of 750 microns for a RO membrane, can reach a width of 2000 microns for UF membranes in the case of more concentrated solutions more viscous or food industry. Obviously in this the second case it reduces the membrane area per unit volume. The greater cost of spiral membrane are its terminals. If you need to use multiple modules can be therefore appropriate to put the modules in a single pressure vessel. In this case up to 6 modules alloggiati can be in a single vessel. The limit, the maximum number of modules in series is the minimum flow rate of the transverse flow for the last module. There are a number of limiting factors the use of membrane modules: the maximum feed flow rate, the maximum flow rate of load, the maximum operating pressure and the maximum temperature. The supply flow rate must guarantee not to turbulent flow conditions. The use of each membrane module limits It is supplied by the manufacturer.

#### hollow fiber modules

The module resembles a heat exchanger tube bundles (Figure 2.6). power is entered into the mantle, it passes through the fibers and then the permeate is collected on the tube side. This module has the advantage of being able to be controlled with pressure differences modest. Currently, there are no forms to fiber reverse osmosis hollow. The degree of packing can reach 30,000 meters squared and meters. The hollow fibers are contained in a container of PVC, aulico or reinforced plastic. This type of membrane module is used for multiple applications both for separating gas and liquid phases components. When used for gas separation the fibers have thicknesses of less than 100 microns and a length of several meters. In the case of Ro the fibers are at most 2 meters long and in the case of hemodialysis patients are about 25 cm long and each module contains up to 10000 fibers. These membranes have a greater permeability compared to the spiral modules or plates since it is possible to eliminate all surface defects, this obliges to adopt the operating flows lower than those for others. Types of modules, also the presence of bundles of closely spaced tubes makes the module vulnerable to problems fouling. The hollow fiber modules predominate the hemodialysis market. The blood passes through tubes while the dialinato passes in countercurrent through the mantle.

### tubular modules

This module is an extension of the hollow fiber bundles of pipes that have a diameter of up to 25 mm (Figure 2.7). It shall, in this case of the perforated rigid pipes staying on the surface Inside the membrane. In this case there is of very low membrane area per unit volume but a large section of the supply passage which allows you to also treat a fluid that It contains suspended solids or non-Newtonian fluids such as those that can be found in industry food. For their performances can do without pre-filtration treatment. In each module can find accommodation up to 1,000 tubes.

### Selection criteria of the membrane module

Via are factors that determine the choice of the membrane module, among them the main ones are: concentration of suspended solid, fouling, ease of cleaning, the supply viscosity, the pressure loss, the manutensilità and cost. In Table 2.1 the advantages and disadvantages of different modules are reported together with the technologies for which they are used. In addition, in Figure 2.8 listed the hold-up liquid with the different types of module, as a consequence of distance to which they can be placed the different elements. The volume of the liquid contained in each module (wold-up) is particularly important when dealing with high-value products added.

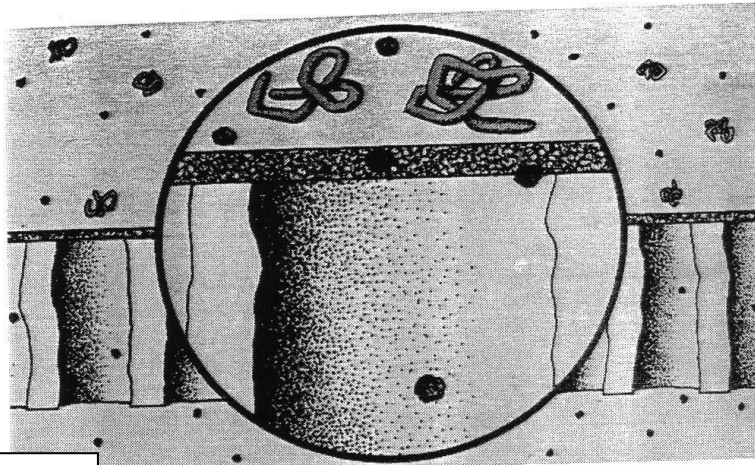


Fig 1 A

2.1b 2.1a

Schematic representation of the ultrastructure of an asymmetric ("skinned") membrane. Particles do not pass through the skin and do not enter the filter body. (Scale is distorted for illustrative purposes. In reality, the "skin" layer is only about 0.1–0.5  $\mu\text{m}$  thick, while the rest of the body of the membrane may be 100–200  $\mu\text{m}$  thick.) (Source: Millipore Corporation, with permission).

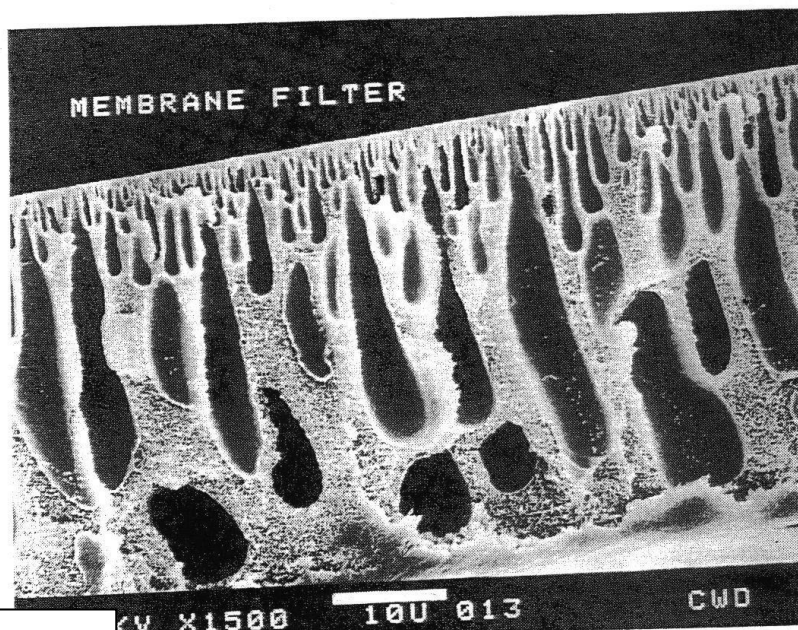
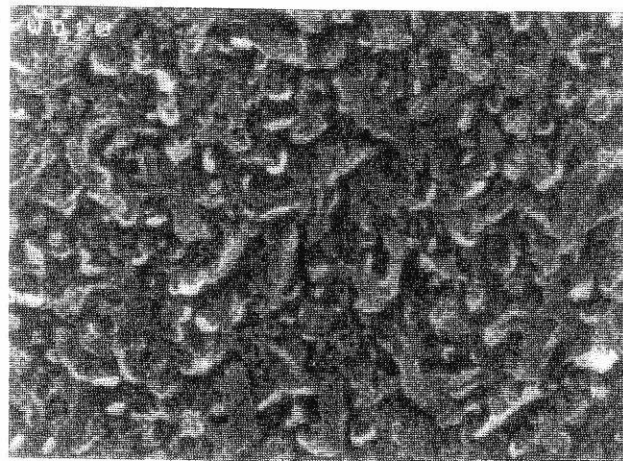


FIGURE FIGURE

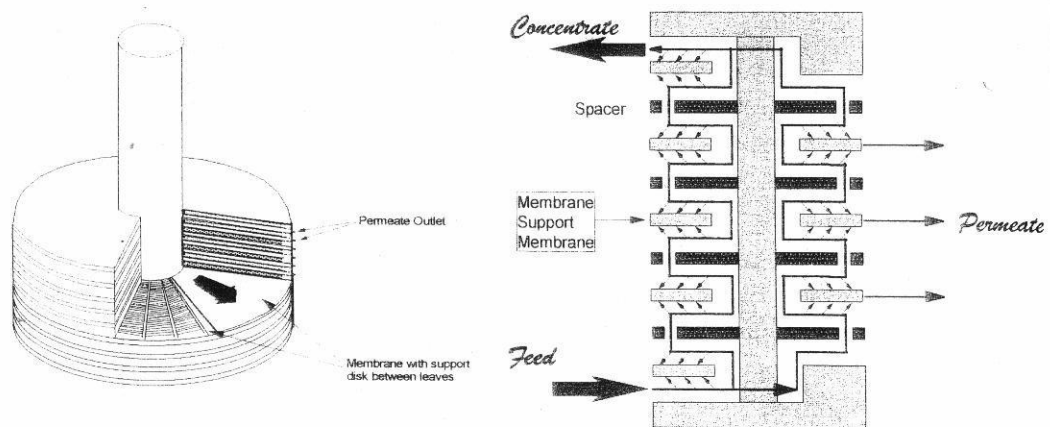
Figure 2.1b Electron micrograph of the cross section of an asymmetric polysulfone ultrafiltration membrane (Source: Cuno Inc., with permission).



**FIGURE 2.2**

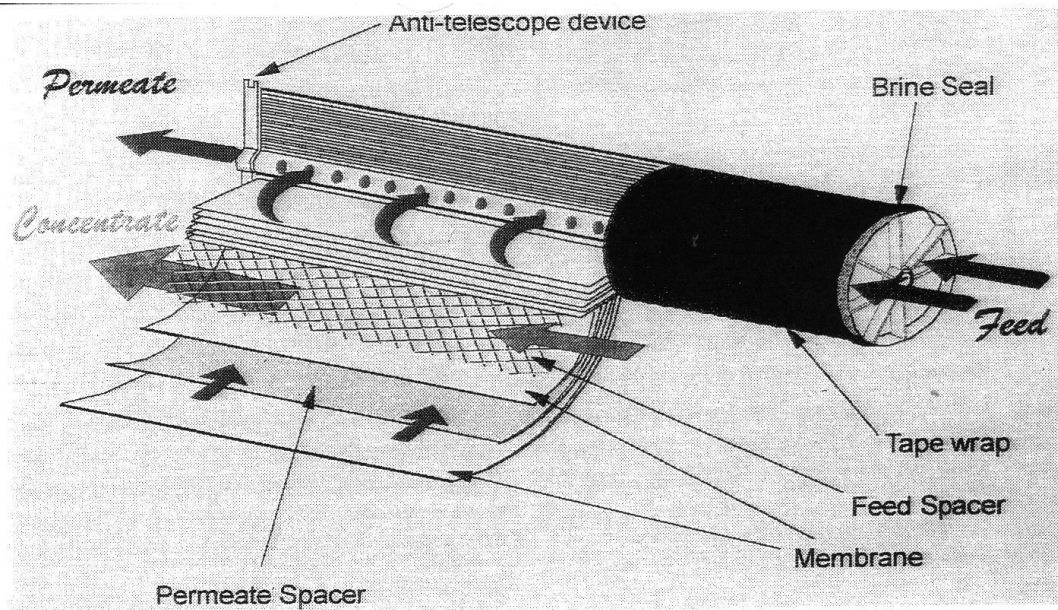
*Scanning electron micrograph of the surface of an interfacially polymerised membrane produced by Film Tec (approximately 2 by 5 microns in size). Interfacial membranes exhibit a complex surface structure, unlike more traditional membranes which are totally smooth at this magnification. Some of the high flux characteristics of interfacially polymerised membranes has been attributed to this roughness.*





**FIGURE 2.3**

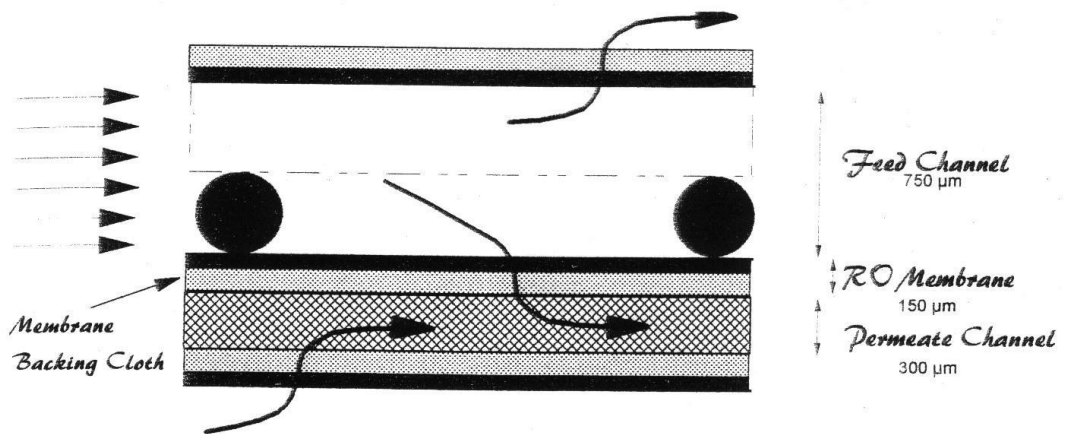
*Schematic diagram of plate and frame devices.*



**FIGURE 2.4**

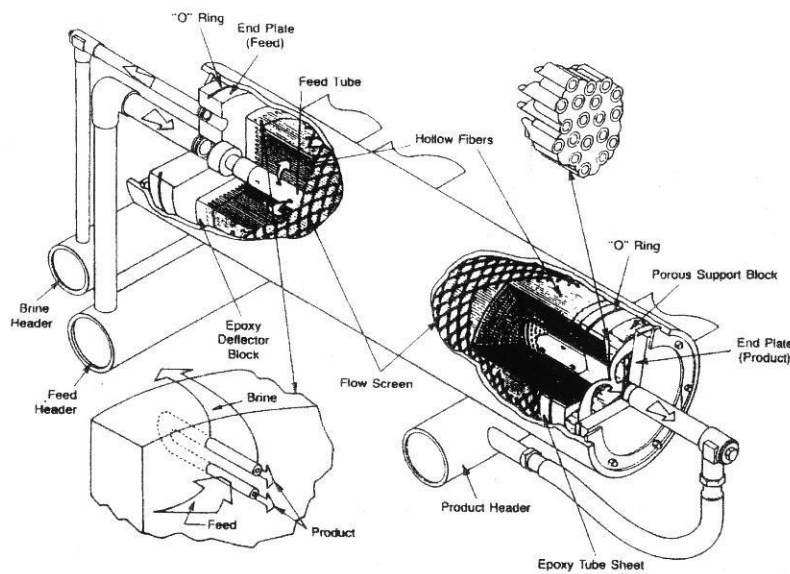
*Figure 3.3-1* Schematic of a spiral wound element showing cut-away section of internals.

Fig 4



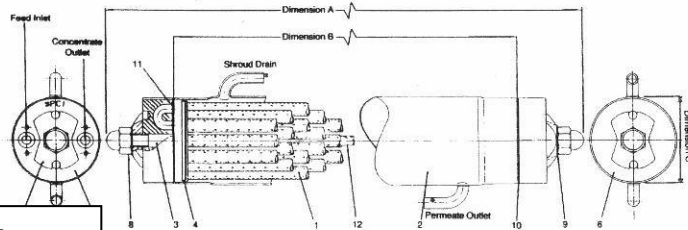
**FIGURE 2.5**

Schematic of section through a reverse osmosis spiral highlighting channels and size scale



**FIGURE 2.6**

Schematic of Permassep® hollow-fibre RO element. A particular feature of the device is that the flow is from the outside into the lumen of the fibres where it is conducted to one of the ends. The large elements are about 200 mm in diameter, and 1.5 long. (Courtesy of DuPont)



**FIGURE 2.7**

Illustrated is a tubular system from PCI. The assembly consist of 18 stainless steel tubes which houses tubular membranes of 12.5 mm diameter. The tubes are either 1.2 or 3.66 mm in length. The total membrane surface area is 0.9 and 2.6 m<sup>2</sup>. Depending on end fitting the flow can be in series or in parallel. (Courtesy of PCI Membrane Systems Ltd)

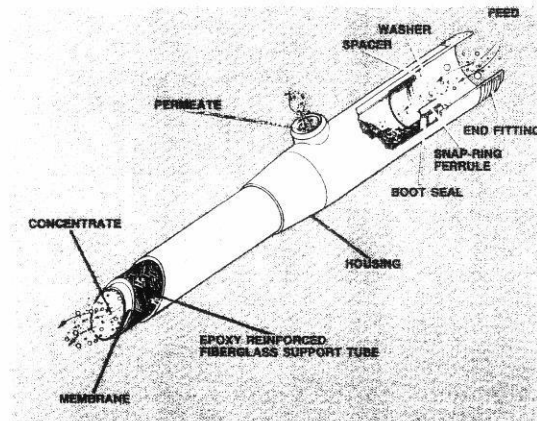
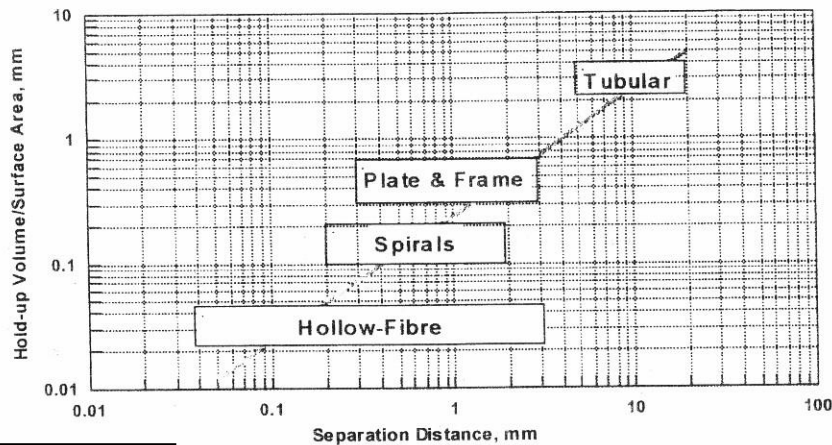


Figure 3.5-2 Illustrated is an element for a single tubular ultrafiltration membrane with 1 inch diameter made by Koch. (Courtesy of Koch Membrane Systems)



**FIGURE 2.8**

*Hold-up volume for various membrane packages.*

**TABLE 2.1**

*Advantages and disadvantages of membrane packaging. The last column indicates the technology which uses the various packaging types (technologies in brackets indicate its availability in the specified format but it is not a major part of the market).*

PACKAGE TYPE	ADVANTAGES	DISADVANTAGES	TECHNOLOGY
<b>Flat Sheet</b>	<ul style="list-style-type: none"> <li>• Wide choice of membranes</li> <li>• Can be cleaned by disassembly</li> <li>• Low energy requirement</li> </ul>	<ul style="list-style-type: none"> <li>• High cost</li> <li>• Replacing membrane is time consuming</li> <li>• Can have seal problems</li> </ul>	D,ED MF, UF (NF), (RO), (HD)
<b>Hollow-Fibre</b>	<ul style="list-style-type: none"> <li>• Very compact system</li> <li>• Low liquid hold-up</li> <li>• Low capital cost</li> <li>• Backflushable</li> </ul>	<ul style="list-style-type: none"> <li>• Easily fouled with particulates</li> <li>• Not suitable for viscous systems</li> <li>• Limited range of products available</li> </ul>	GS, HD UF, MF, RO
<b>Spiral Wound</b>	<ul style="list-style-type: none"> <li>• Low hold-up</li> <li>• Compact system</li> <li>• Wide range of materials</li> <li>• Wide range of sizes</li> <li>• Low capital cost</li> </ul>	<ul style="list-style-type: none"> <li>• Can have dead spots</li> <li>• Cannot be backflushed</li> </ul>	RO, NF, (UF), (ED)
<b>Tubular</b>	<ul style="list-style-type: none"> <li>• Can tolerate feeds with high suspended solids</li> <li>• Can work with viscous and non-Newtonian fluids</li> <li>• Easy to clean mechanically</li> </ul>	<ul style="list-style-type: none"> <li>• High energy requirement</li> <li>• High capital cost</li> <li>• Large space demand</li> <li>• Disassembly long</li> <li>• High hold-up</li> </ul>	MF, UF, NF, RO

## CHAPTER 3

### GENERAL EQUATIONS MEMBRANES

In the following discussion it will be made two important assumptions. The first is that the solvent behaves according to the law of ideal Roults, the second concerns the incompressibility dell'liquido.

In the cell shown in Figure 3.1 we have an ideal membrane permeable only to the solvent which separates the pure solvent from the solvent with dissolved solutes.

Under these conditions, at pressure P and temperature T constant, the water chemical potential (which is the most commonly used solvent, and will be indicated with the index w) is such that

$$\mu_{w0} - \mu_w = -RT \ln x_w \quad (3.a)$$

where with  $\mu_{w0}$  It indicates the potential of pure water, with  $\mu_w$  that of water in a solution with molar fraction equal  $x_w$ .

since  $x_w < 1$  The term in equation 3. a second member is positive, so  $\mu_{w0} > \mu_w$ . There difference of these quantities is the pushing force of the separation process and determines the passage of water through the membrane, which will pass spontaneously from the solvent zone pure to that of less pure solvent. This process would continue until all the pure solvent, as the solution can never reach the condition  $x_w = 1$ .

The phenomenon is however counteracted by the hydrostatic head. The solvent passing through the membrane raises the level of the wing on the side of the solution and lowers the one on the solvent side pure. The pressure difference that is created participates on the overall calculation of the difference of chemical potential as

$$\mu_{w0} - \mu_w = -RT \ln x_w - \int_P V dP \quad (3.b)$$

V with partial molar volume of water. In equilibrium conditions that we

$$\mu_{w0} - \mu_w = 0 = -RT \ln x_w - V \pi \quad (3.c)$$

with  $\pi = RT V^{-1} \ln x_w$  osmotic pressure of the solution, valid in the case of ideal solutions very diluted. Nothing changes if instead of the pressure difference due to the hydrostatic head we consider a pressure  $P^*$  externally applied, for example by a pump (Figure 3.2).

In general, to simplify the discussion, the chemical potential of the solvent gradient is expressed in terms of the pressure difference, while the chemical potential gradient of the solute in terms of concentration gradient. The variables used to characterize the performance of a membrane are two, the solvent flux  $J_w$  and the solute flow  $J_s$  which passes through it, equal to the volumetric flow or mass of solvent and solute that pass per unit of time a equal surface area of membrane unit.

The solvent separation is expressed through the recovery  $Y$ , equal in the case of continuous processes

$$Y = J_w A F_{f-1} \quad (3.d)$$

with  $A$  total area of membrane and  $F_f$  feed flow rate. In the case of discontinuous processes, definition changes slightly, and becomes

$$Y = V_{f-1} \int_t J_w A dt = V_p V_{f-1} \quad (3.e)$$

with  $V_f$  volume of the initial solution to be treated and  $V_p$  total volume of permeate obtained.

The separation of the solute due from the membrane is expressed through the rejection, equal to

$$R = 1 - (C_p / C_f) \quad (3.f)$$

with  $c_p$  and  $c_f$  concentrations respectively in the permeate and in the feeding of solute considered.

It is defined as a fall of  $\Delta J$  flow  $w = J_w(t) / J_w(t = 0)$  the decrease in the permeate time through the membrane.

Finally, it is called with TMP (transmembrane pressure) the pressure drop across the membrane, defined as

$$TMP = (P_f - P_p) - (\pi_f - \pi_p) \quad (3.g)$$

with  $P_f$  and  $\pi_f$  operational and osmotic pressure on the membrane surface, the feed side and  $P_p$  and  $\pi_p$  operational and osmotic pressure on the surface of the membrane, the permeate side.

The permeation models vary according to the phenomenon of transport through the membrane. In the case of predominantly convective transport (MF, UF), the most common model is to Hagen-Poiseuille (Figure 3.3) for laminar flows, amounting to

$$J = \frac{d_p^2 \epsilon P}{32 \mu} \quad (3.h)$$

with  $J$  total flow, the sum of  $J_w$  and  $J_s$   $d_p$  pore size, the degree of porosity  $\epsilon$  coverage on the membrane surface, the applied pressure  $P$  and  $\mu$  the viscosity of the liquid.

Another case is the diffusive transport, described by the solution-diffusion model (typical for the processes RO). In this case it is assumed that the membrane is non-porous, that the solvent and the solute is It dissolves in the membrane phase, that the spread of the often interacts not that of the solute and vice versa, and that the concentration gradients are the result only of the applied pressure. As previously mentioned, it is considered decisive for the permeation of the solvent pressure gradient, and then write

$$J_w = \frac{D_{wm} V_w}{RT} \frac{TMP}{A} \quad (3.i)$$

$D_{wm}$  diffusivity of the solvent in the membrane,  $V_w$  the molar volume and permeability  $A$  water. For the solute considering the change for negligible pressure and will write that

$$J_p = \frac{D_{sm} k_{sm}}{B} (C_m - C_p)$$

$D_{sm}$  diffusivity of the solute in the membrane,  $k_{sm}$  partition coefficient,  $C_m$  and  $C_p$  there concentration of the solute on the membrane feed side and permeate side respectively, and the  $B$  permeability of the solute.

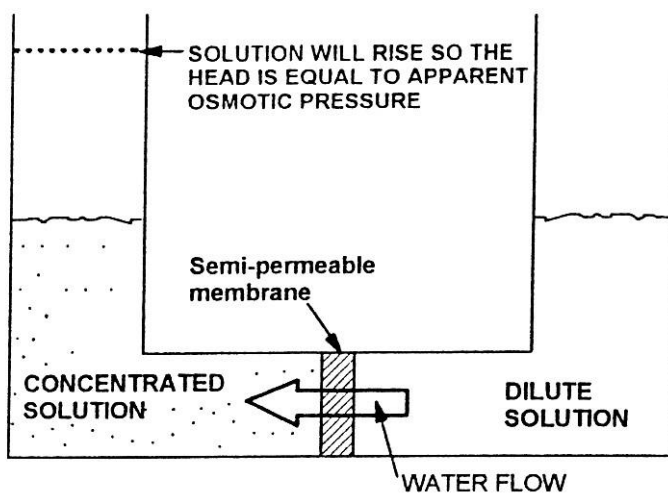
The equation can be rewritten as 3.h and 3.i



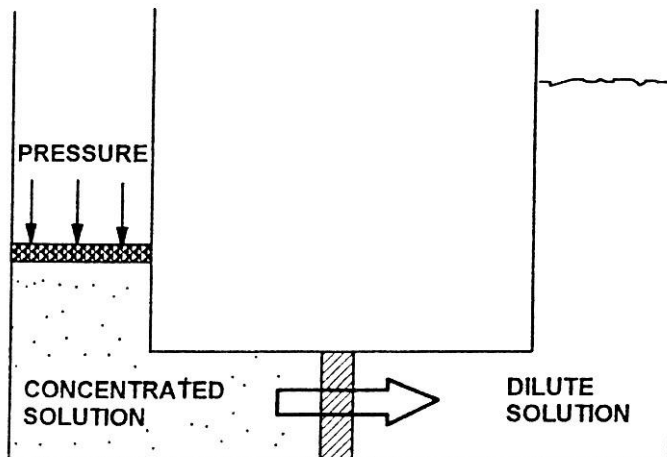
$$R_{-1} = 1 + (B / A) \text{TMP}_1$$

(3.j)

It may be noted that as for TMP goes towards infinity, the rejection R tends towards the unit value  
(Complete rejection of the solute).

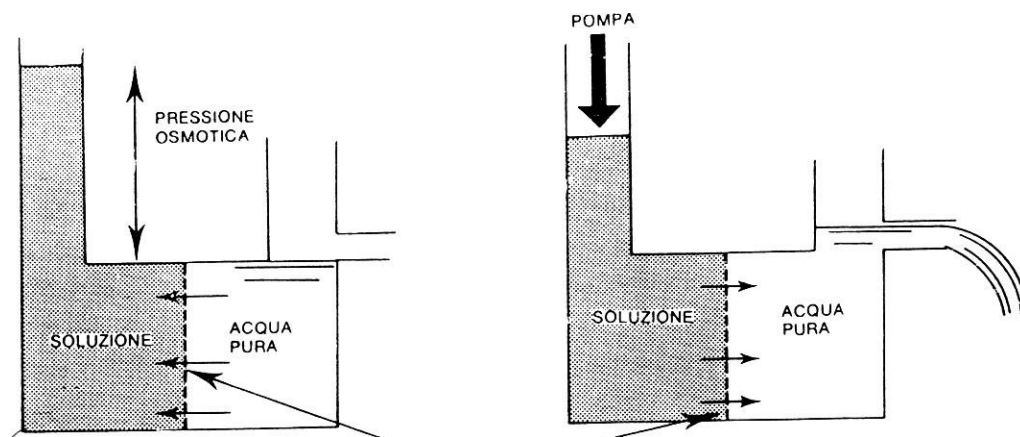


## OSMOSIS

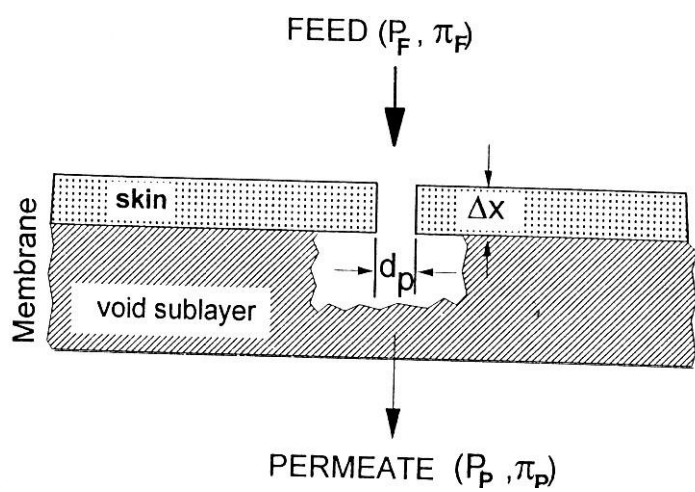


## REVERSE OSMOSIS

FIGURE 3.1: Osmosis and reverse osmosis.



**FIGURE 3.2:** Osmosis and reverse osmosis in the case of external pressure applied to the system.



**FIGURE 3.3:** The Hagen-Poiseuille model.

## **CHAPTER 4**

### **TECHNOLOGY-BASED MEMBRANE PROCESSES**

#### Technologies based on the pressure gradient

Membrane processes of wider use are those that perform in fact a filtration solution / suspension to be treated under a pushing force consists of a pressure gradient. They are distinguished by the pore size of the membrane and consequently to the gradient of pressure that must be applied (see Table 4.1). As the pore size and the pressure to be applied such technologies have arisen with the name of: microfiltration (MF), ultrafiltration (VF), nanofiltration (NF) and reverse osmosis (RO). While the MF can separating visible sized particles, such as biological cells, the RO regards the separation of origin of saline ions and small organic molecules. These two technologies are the uprising UF the separation of macromolecules and NF more similar to the RO, but, as based on membranes more permeable, capable of retaining salts and organic molecules of greater dimensions, for example divalent ions. Other features characterizing these different technologies are harvested in Tables 4.1 and 4.2. The RO was developed especially for seawater desalination, for its ability to prevent the passage through the membranes of the salts and to obtain as the permeate water to a saline content compatible with its potability. Subsequently this type of technology has been applied both to obtain water from discharge into drains starting from wastewater, such example of percolation water from open loop landfills, or for concentrating a liquid, such as the juices. The most interesting aspect of this second type of application is the ability to obtain a low-temperature concentrated fluid without having to resort to thermal processes, such as the evaporation that would lead to degradation of some components that guarantee the quality the final product.

The NF allows a more gentle separation of the RO and is therefore preferable in many cases in which the separation of larger molecules goes hand in hand with the need to reduce costs.

This technology has arisen for softening water as an alternative to lime process hydrates and is then developed for a variety of applications such as: removal of sulfates, color removal, partial desalination of waste water, removal of pesticides, concentration of sugars.

The UF does not allow the separation of salts, but that of biological macromolecules, for which it is a particularly it applied in the food industry technology, in particular in the milk industry.

Finally, the MF has found its first application as a technology for clarification processes,

for its ability to eliminate micron or submicron particles difficult to separate through the traditional filtration. This technology is finding an increasing use recently growing to improve drinking water quality by removing the pathogens resistant to chlorine treatments.

#### Technologies for the gas separation

For one of the first applications of this technology is a silicone rubber is used for O<sub>2</sub> to produce medical uses. Currently it generally makes use of hollow fibers. Monsanto developed in the 70s of the membranes of hollow fibers polysulfonico material to recover hydrogen from gas effluents in the production of ammonia. The separation is based on two principles: Knudsen diffusion in the pores of the membrane and the capillary condensation in the pores. For the application of the first principle it is necessary that the mean free path of the species from separation is less than the pore size. In permeated it will enrich the gas that has a path mean free smaller and therefore a lower atomic weight. The separability between 2 components in this case proportional to the square root of the molecular weights. Unlike gas vapors have a higher permeability through a membrane, therefore they can be separated both for drying wool side by eliminating the water vapor both for removing organic vapors which may thus it is concentrated and possibly reused.

#### **TECHNOLOGY WITH ELECTRIC POWER pushing**

The electrodialysis ( "ED") is a membrane process that allows the removal of ions from a solution using ion-selective membranes. This is done by passing the solution between two membranes to which an electric field is applied. The latter determines the passage towards the respective electrodes. Using a membrane permeable to anions on one side and a permeable to other cations, the ions can be removed by a current and concentrated in another (see Figure 4.1). The big step forward in this technology was done when they are been realized multiple compartments (see Figure 4.2). With the reduction of the costs of investment.

Most electrodialysis application has been made in water purification both from sea from other parts sources. The ED can also be used to desalinate partially foods such as milk, juices etc., and to recover electrolytes such as silver and nickel. The membranes used are thick, non-porous. The essential element is the ion-exchange membranes formed from matrix

polymer with electrically charged groups. The membranes that allow the passage of ions positive are called cationic, those who leave go negative ions are called anionic. Even for these membranes there is the problem that fouling can be reduced by the reverse electrodialysis process (EDR), ie reversing the polarity. In this way the deposit which is formed on the membranes was dissolved and dispersed. The configuration of the module can be planar or tortuous flow; in the first case the flow takes place between two membranes and the speed is low, less than 0.1 m / s, in the second case the flow is made tortuous to increase the mixing and speed is greater between 0.1 and 0.5 m / s. Finally, you may also adopt a spiral form with a electrode in the center and the other outside, thus having a radial electric field. The energy required to the electrodialysis operation is that required by the pumps that operate on different currents and one that acts to transfer the ions, it is equal to:

$$E = \frac{1}{2} VF \cdot \frac{1}{Q}, \text{ Joule / g equivalent} \quad (4.a)$$

The phenomenon of polarization limits the intensity of the electric field which in the case of desalination salt water can not exceed 1000 A / m<sup>2</sup>. The electrodialysis process was recently applies for the sodium chloride chlor-alkali plants (see Figure 4.3). In this case, adopts a PTFE membrane made hydrophilic docking at the group fluorinated sulfuric acid.

### **pervaporation**

In the pervaporation process it is fed a liquid solution and the component which passes through the membrane changes state giving rise to a permeate in vapor phase. The membrane used in this case is asymmetrical on the type of those used for the RO. The permeability of different components through the thin layer of the asymmetric membrane gives rise to the selectivity Process. Evaporation at downstream of the membrane requires the steam that comes warm it from transferring such heat across the membrane. A downstream of the membrane a carrier gas or vacuum depart permeate. The gas composition is permeated significantly different from that which would be determined from equilibrium vapor and liquid. In case azotropici of systems is so possible to overcome dell'azotropo. A typical application case is the dehydration of alcohols and other solvents. Typically if the supply current contains the 5% of water, the permeate will count the 5% organic.

## MEMBRANE PROCESSES WITH THE CONCENTRATION AS FORCE pushing

### Hemodialysis

And 'This is the process of purifying the blood of people who have big problems kidney. Of even made the kidney is constituted by a membrane that filters out blood purifying it from metabolites of low molecular weight such as urea and creatine. When the human kidney is no longer able to carry out this task, the patient is subjected to the so-called dialysis ie the washing of the blood by means of an external device consists of a membrane module with hollow fibers. The blood is sent inside of the hollow fiber while outside in countercurrent is passed a said dialysate solution typically consists of acetate with a low content of potassium (see Figure 4.4). This equipment was developed in the 40s by a chemical engineer, Kolff, and applied in the 60s. Recently the dialysis equipment are preceded by a UF (hemofiltration) that removes larger metabolites. This is the membrane process that has a higher turnover.

### diafiltration

In some ultrafiltration applications, concerning for example the purification of proteins will It may be a solute concentration only as to excessively increase the viscosity of rejected and obtain a permeate, which is a recovery factor, very low. In these processes it is important not to concentrate a component but eliminate together with the solvent provided with the solute low molecular weight. In this case use is made of a membrane process called diafiltration, in which is fed water in the starting solution to compensate for the water that permeates through the membrane. The diafiltration operation may be carried out in continuous and in discontinuous (Fig. 4.5). In the batchwise process (DD) of the starting solution is purified with respect to product which permeates through the membrane and the volume is greatly reduced, it is then adding the water and there is a further filtration. A simpler plant layout is that of Continuous diafiltration process (CD) (Figure 4.6). In this case the solvent is added continually rejected in order to recompose always the same dilution of the solution of departure. If you define  $VD = \frac{\text{solvent flow added}}{\text{current flow initial}}$  one can assess what is the concentration over time in the feeding of which a solute with reaction coefficient equal to 0, by means of the report:

$$c(t) / c(t = 0) = \exp(-Vd) \quad (4b)$$

If the reaction coefficient is  $R_j > 0$

$$c(t) / c(t = 0) = \exp(-Vd(1 - R)) \quad (4.c)$$

$Vd$  increases and decreases in the  $Y$  recovery involve both increases the removal of solutes supply (see Figure 4.7). You must therefore carefully choose both values, Whereas the operating limits (maximum amount of solute removable in function of  $Y$ ) and the costs (Amount of fresh solvent to be used  $Vd$ ).

Normally volume work of constant power, ie the volume of solvent added is equal to that of the permeate. In Table 4.3 there is an example of a continuous-filtering a solution aqueous forage. It should be noted that increasing of the permeate volume is a reduction of solutes of low molecular weight and an increase in the concentration of proteins.



TABLE 4.1

*Typical operating parameters and membrane materials used for pressure driven processes*

Process Technology	Material	Typical Operating Range		Rejected Species
		Pressure	Recovery	
Microfiltration	Polymers Ceramics Metals	0.5 - 2 bar	90-99.99	Bacteria, Silts, Cysts, Spores
Ultrafiltration	Polymers Ceramics	1 - 5 bar	80-98	Proteins, Viruses, Endotoxins, Pyrogens,
Nanofiltration	Polymers	3 - 15 bar	50-95	Sugars, Pesticides
Reverse Osmosis	Polymers	10 - 60 bar	30-90	Salts, Sugars

TABLE 4.2

*Table 2.2.3 Typical dimensions and conditions in membrane filtration devices (the RO figure refers to that of a typical spiral wound element, while the UF and MF figures refer to that used in hollow-fibre devices). These figures are derived from devices designed to treat thin waters (i.e. systems with viscosity close to that of water).*

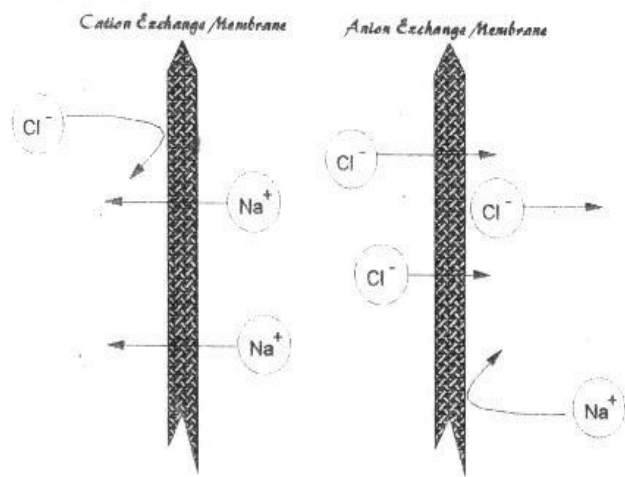
Technology	Distance Between Membranes cm	Cross-flow Velocity cm/s	Flux L/m <sup>2</sup> /hr
Reverse Osmosis	0.05	10 - 25	40 - 90
Ultrafiltration	0.1	25 - 100	50 - 150
Microfiltration	0.15	100 - 300	100 - 200

$V_D$	Volume ( $V_P$ ), L	Protein % w/v	Lactose % w/v	NPN* % w/v	Ash % w/v	Total Solids % w/v	Protein in Solids (% d.b.)
0	0	0.4	5.0	0.2	0.68	6.28	6.4
1	100	0.4	1.84	0.074	0.306	2.62	15.3
2	200	0.4	0.68	0.027	0.14	1.244	32.1
3	300	0.4	0.25	0.01	0.062	0.72	55.4
6	600	0.4	0.012	0.001	0.006	0.419	95.5

\*Nonprotein nitrogen

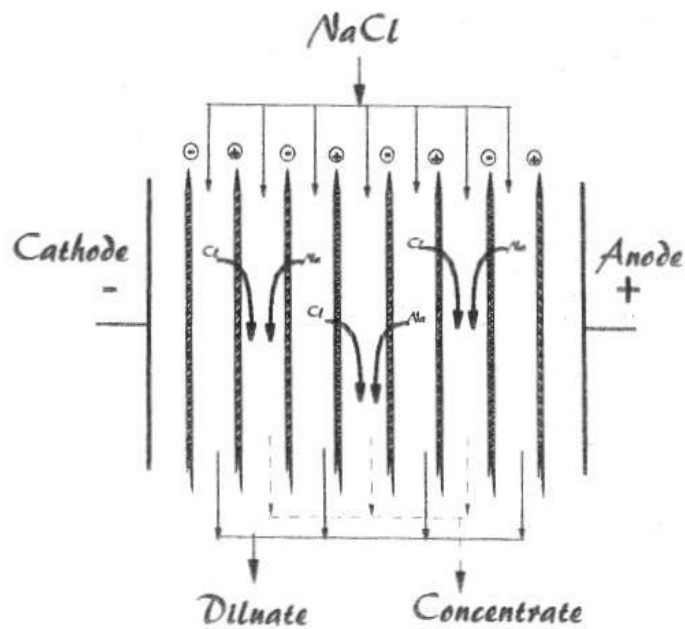
Concentration of solutes calculated using Equation (7.15)

TABLE 4.3: Example of a diafiltration process of  $V_P$  function.



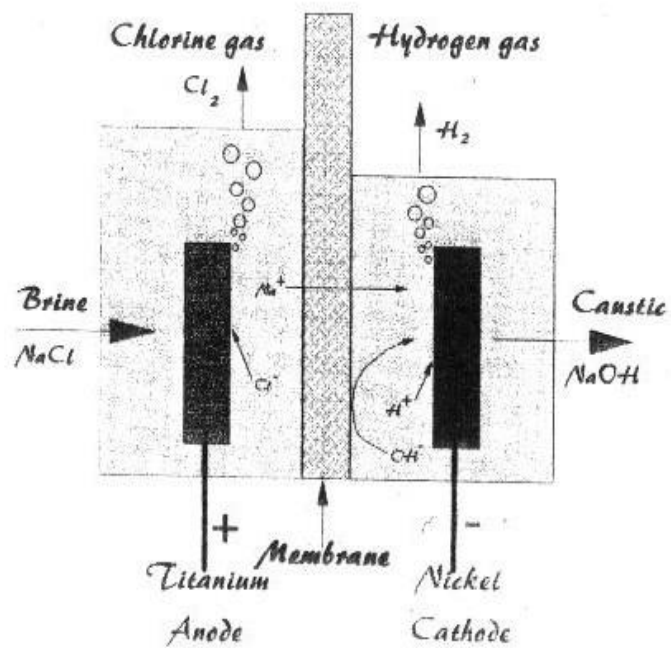
**FIGURE 4.1**

*Diagrammatic cross-section of electrodialysis cell working on sodium chloride*



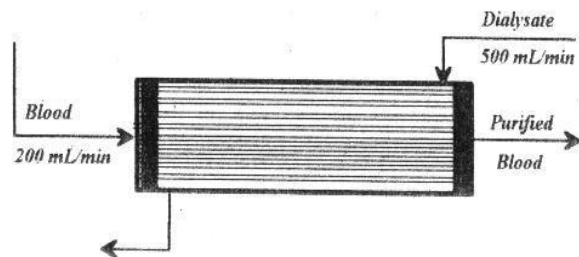
**FIGURE 4.2**

*Schematic of electrodialysis stack. Typically, there are several hundred pairs of membrane*



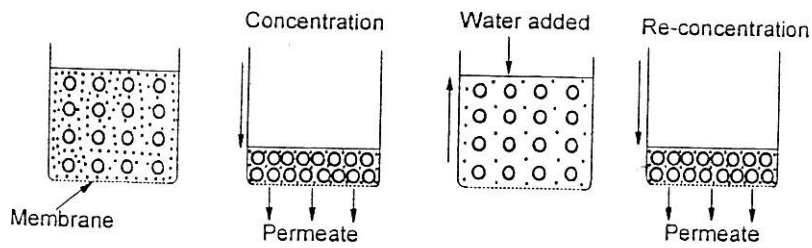
**FIGURE 4.3**

*Schematic of membrane cell for production of chlorine and caustic.*

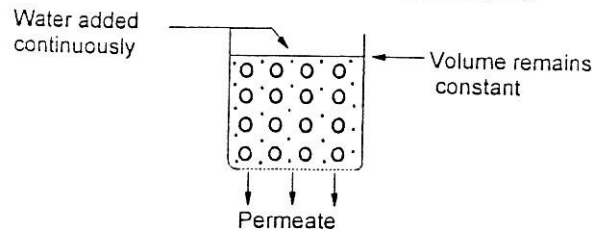


**FIGURE 4.4**

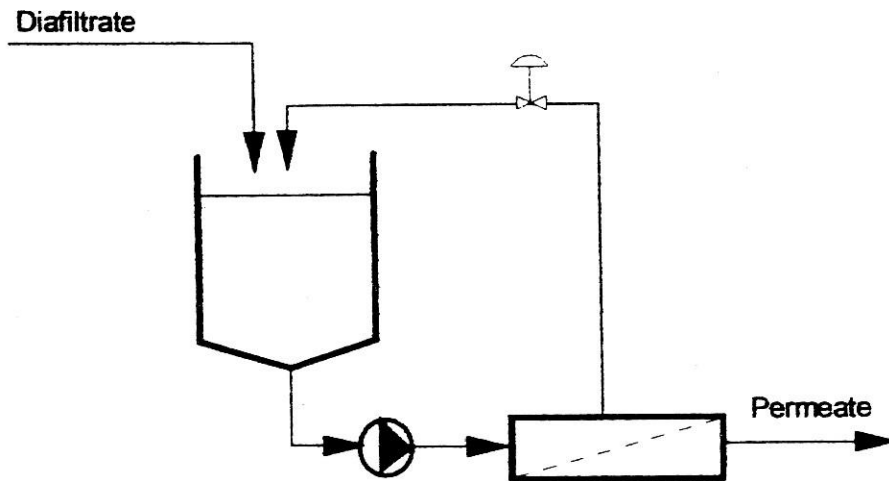
*Schematic of haemodialysis unit. Blood is passed along fibre lumen, and solutes are exchanged with diafiltrate*



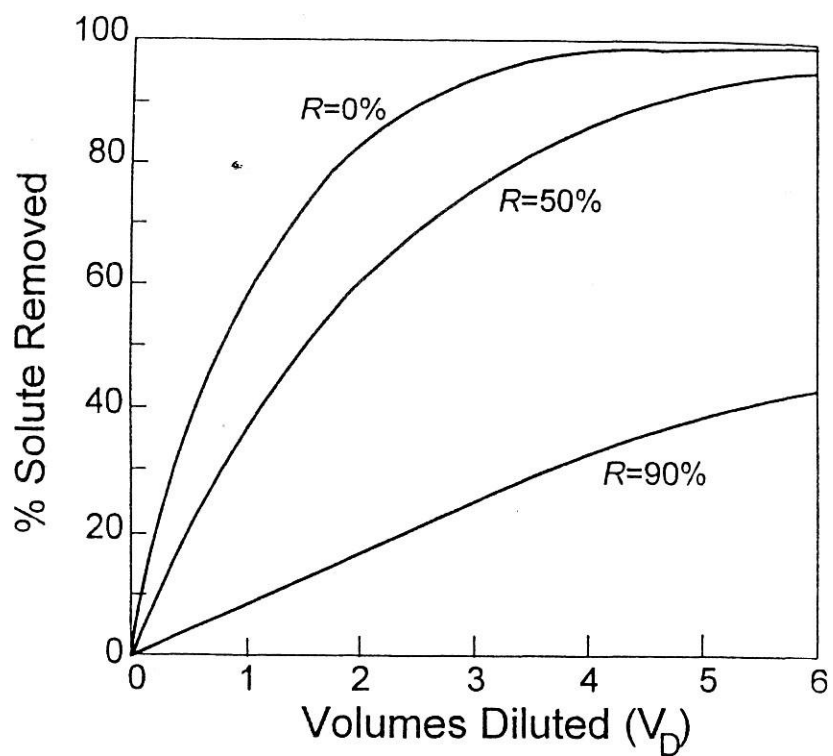
CONTINUOUS DIAFILTRATION (CD)



**FIGURE 4.5:** Diafiltration continues (above) and discontinuous (below).



**FIGURE 4.6:** Planting Scheme for continuous diafiltration.



**FIGURE 4.7:** Results of the purification of corrente recovery as a function of  $Y$  (here  $R$ ) and of the dilution volume used.

## **CHAPTER 5**

### **THE FOULING MEMBRANES**

The thermodynamic model of the membrane separation phenomenon has a big problem to be Valid only for very dilute solution. The reason for the restriction resides in the fact that in case of dilute solutions, the amount of solvent that is separated and removed to the solution does not imply a sensitive reconcentration of the pollutants, and therefore does not alter the separation conditions.

In Figure 5.1 it is shown a phase diagram of a hypothetical colloidal solution. The state of aggregation of the solution strongly depends on the stability and the concentration of pollutants. The stability of a solution is determined by many factors such as for example the temperature, nature and the strength of interaction between the solvent-solute and solute-solute.

Figure 5.1 shows the existence of multiple phases. A low concentration and high stability are the phase gas, which is the phase analyzed by the thermodynamic model and in which the solute is in a state dispersed. In this manner, the solute is free from interactions by the solvent.

Destabilizing this solution, you enter the field of aggregate phase, where they begin to form, in a sparse manner, the first mini-aggregates of solute.

Increasing the concentration of solutes and overcome the so-called concentration of gelling  $c_g$  It introduces in other two zones. The first, more stable, is that of the liquid phase, where the colloids, which constituting the solute, we are organized to search for equilibrium positions in the solvent.

The most unstable area is instead referred to as the gel phase, where long chains of solute aggregates form and begin to bind between them. The web that is formed has elastic characteristics and in able to attract and capture other colloids or aggregates to increase its size.

Finally, at high concentrations, above the solidification concentration  $c_s$ , We meet the phase solid, which crystallizes in a more or less dispersed in the solvent.

The forces acting on the particle during the tangential separation process is illustrated in

Figure 5.2, in the case of a neutral membrane. In the case of electrostatic membrane, we also the forces of attraction and electrostatic repulsion on the ions.

The convective force is due to the drag of the particle in the solution, which is pushed tangentially on the membrane surface. This force is counteracted by the frictional force.

Of greater importance are the forces perpendicular to the membrane. The first is the pushing force date from TMP applied, which seeks to induce the solvent to pass through the membrane. The solvent

flowing toward the diaphragm induces a convective force towards the membrane itself. The forces of suspension, which seek to raise the particle from the membrane surface, and reintroduce in the current power, seek to counter the first two.

In industrial separations you want to maximize the production of permeate. All this leads to want to push as fast as possible large amount of solvent through the membrane, and then it tends to increase the force pushing TMP. The consequence of this action is a strong decrease in the suspension forces and the consequent localized solute adhesion on membrane surface. In fact, the solute is dragged in a manner by convective mass towards the membrane, but unlike the solvent it is stuck on the surface of the same. It will create the Consequently a concentration gradient between the membrane surface, very concentrated in solute, and the power supply flowing above it, the more diluted. The higher the solvent passage through the membrane, the greater will be this concentration gradient. The formation of concentration gradient is called the membrane polarization phenomenon.

The polarization of the membrane decreases the permeate flux. In fact, on the surface of Power of the membrane creates a higher concentration of solutes which leads to a greater osmotic pressure. As a result, the solvent which is separated on the permeate side try to pass through the membrane so as to dilute the concentrate on the opposite side (see Figure 5.3).

If the solute is not removed from the membrane more, it is stratified on its surface. There ravvicinanza of solute-solute particles and the increase of their locally destabilize density the solution and significantly increase their concentration. At one point, the solute on membrane is transformed into the gel phase. This phenomenon leads to the so-called fouling reversible.

If there is a gel phase on the membrane, but the polarization is not stopped, at a certain point form on the membrane the solid phase. The solid phase may locally crystallize on the surface of the membrane, but it can also be formed at the entrance of the pores. The consequence is the formation of a highly impermeable crust that clog the pores, and leads to irreversible fouling of the so-called membrane.

With  $F_p$  permeate flow rate measured at the output of the membrane flux, the fouling on the membrane It says strong when you look at the profile  $F_p - P$  a sharp deviation from linearity from a certain point. Fouling is called weak, if the deviation occurs immediately (see Figure 5.4).

The two different behavior is due to the stability of the solution. In strong fouling, we can work in conditions free from fouling for a certain range of operating pressures. In fouling weak, the polarization occurs immediately and any pressure operates is creates more or less fouling. Obviously, the weak form of the fouling is the least desired.

One way to decrease the gelation of the membranes is to increase the forces of Suspension. Since this force is closely related to the applied force convective power supply, the membrane processes are operated with high flow rates of feeding regime turbulent. In contrast to the laminar flow, the presence of turbulence prevents that the solution can stagnate on the membrane surface. The turbulence is encouraged with the presence of so-called spacers, which are of the networks on the membrane surface and try to deflect, to equal to the static mixer, the natural course of flow and shake the most possible.

The greater the strength of the suspension, the higher the TMP will be applicable and the flow rate of permeate produced, before warning gelling phenomena.

In addition, from 5.1 Ffigura one can observe that more stable solutions can have concentrations of solute more before reaching the critical concentrations of gelling or solidification.

So it has to stabilize and de-concentrate solutions before you process them on the membranes.

One way to pretreat solutions efficiently it is the clotting process, as reported by many works in the literature. In addition to eliminating colloids from the starting solution and thus decrease their concentration, the subsequent formation of solute flakes feeding promotes the removal ring road, due to the convective force, away from membrane surface. All this inhibits the formation of the polarization and, consequently, Fouling.

In the case of reversible fouling, the membrane is sufficient to relax temporarily lowering the TMP applied briefly or fueling the system with the pure solvent, to break the gel and completely ripulirne the surface. In this way it operates the membrane rinsing.

In the case that after the relaxation of the reversible membrane fouling has been removed partially, one speaks of semi-reversible fouling: in this case, the gel is not broken up to when it does not work rinsing or until the operating conditions are not drastically reduced.

Finally, in the case of irreversible fouling, it will no longer be possible to remove all the fillings you They are created. Even the so-called wash, made with more or less aggressive chemical agents, can to eliminate all the solid layered on the membrane. The irreversible fouling ruin the membrane



in a definitive manner, and consequently its formation should be avoided. The extent of fouling Irreversible can be measured as a percentage from the reduction coefficient  $Df_p$ .

In the case of reversible fouling, it will follow that  $Df_p \approx 1$ . It should be considered that even without the presence of the fouling there will still be a natural and inevitable aging of the material composes the membrane. This implies that the value of  $Df_p$  decreases over time, although in more slowly and less sensitive than the case with irreversible fouling.

One of the most widely used models is the Resistance model, which links the permeate flow  $J_p$  the force pushing TMP. The two terms, one effect and one cause, are related by what the presence of a total resistance  $R_T$ . We can write that

$$J_p = \frac{TMP}{R_T} \quad (5th)$$

We note that the simplicity of the model is complicated by the difficulty in determining the correlation factor  $R_T$ . With reference to Figure 5.5 and analyzing the possible resistances existing in membrane processes, we can recognize from the membrane intrinsic resistance  $R_m$ , a resistance due to fouling  $R_f$ , a resistance due to the concentration polarization  $R_p$  and a resistance due to the formation of a layer of gel  $R_g$ , all arranged in series. As a result, the 6.a equation can be rewritten as

$$J_p = \frac{TMP}{R_m + R_f + R_p + R_g} \quad (5.b)$$

In this way, we can address the various elements separately.

The resistance  $R_p$  It is due to the polarization concentration gradient. The development of outline concentration along the z axis of the membrane surface is determined by the law

$$c(x) = c_f(z) + \left\{ \left( \frac{J}{D} \right) (dc - x) \right\} \quad (5.c)$$

where  $c_f$  It is the power concentration, the permeate flux  $J$ ,  $D$  the diffusion coefficient,  $dc$  the concentration gradient and  $x$  the distance orthogonal from the membrane. The polarization is  $M$  defined as

$$\text{And } M = \left\{ \left( \frac{J}{D} \right) dc \right\} \quad (5.d)$$

As a rule, compared to the other resistors, the polarization turns out to be negligible, it may have a greater importance in the microfiltration, for which osmotic effects are non-existent: the membrane does not retain much solute for which the difference in concentration between the permeate and Power is small. A polarization developed can subvert this trend.

The intrinsic resistance of the membrane  $R_m$  It is determined by the thickness of the membrane and the size of the pores. To minimize this resistance, the manufacturing industry membranes tries to assottigliarle as possible. The composite membranes were born, they have a very thin asymmetric membrane layer supported on a mechanically resistant matrix. In this manner, the selectivity is discharged to the whole thin and delicate layer of separation overlying, without that the operating pressure can break it.

In the previous chapter we have already been exposed to the Hagen-Poiseuille models and solution-diffusion.

The gelation resistance  $R_g$  strongly it depends on the compactness and the layer thickness gelled. The resistance of this layer may be variable over time, and adapts to changes of operating conditions of the process. Consequently, the dynamic nature of this resistance makes difficult to develop a model.

The simplest approach is that of the film theory, written below.

$$R_g = k \ln (c_g / c_{to}) \quad \text{TMP}_1 = \Phi \text{ TMP} \quad (5.e)$$

with the coefficient equal to  $k = D / AX$ , where  $D$  is the diffusional coefficient of the solution through gel,  $c_g$  the concentration of gelling ec  $c_{to}$  the concentration of the solute in the feed. The first model tells us that the gelation is independent from the force pushing TMP: in effect, a Once the gel is established, it becomes dominant and primarily spread through the layer. In these conditions, the TMP increases are no longer able to ensure linear increases in the flow of  $J$  permeated  $p$ . On the other hand, it is precisely the TMP applied that determines the firmness and thickness the gelled layer: the parameter thus indirectly influence both  $D$  and  $AX$ . Therefore, it is possible to identify a coefficient  $\Phi$  which binds directly to the TMP resistance  $R_p$ .

Finally, the resistance of the fouling  $R_f$ . We have more empirical relationships available. Normally, The fouling develops in a constant manner over time, for which

$$R_f = t_B; R_f = iS_B t \quad (5.f)$$

all relationships are used. Typical equations are irreversible fouling character exponential. The coefficient B is called coefficient of fouling.

In conclusion, for a given membrane we have a constant value of  $R_m$  characteristic. With a determined power, also have a constant value of  $R_p$ . Finally,  $R_g$  and  $R_f$  depend on the operating parameters and therefore vary with the TMP and time.

For selectivity, one of the most widely used approaches is the coefficient based on the relationship written reflection as

$$R_i = 100 (1 - c_{to}/c_p) = \sigma \text{ TMP} / (\text{TMP} + \beta) \quad (5.g.)$$

with  $R_{the}$  rejection of the i-th component,  $\sigma$  the reflection coefficient and  $\beta$  coefficient of fitting. There rejection measured in percentage of the relative amount of solute that fails to pass in the permeate compared to that power. In case of ideal membrane, with a rejection that is 100%, it is It deduced from the second part of the equation that  $\sigma$  and  $\beta$  must apply respectively 100 and 0. In case of real membrane, for which  $\beta$  is different from zero, the rejection will reach the  $\sigma$  value only TMP applied very high. The consequence is that the rejection increases with TMP, up to a maximum value equal to  $\sigma$ .

We have seen how the fouling, reversible or irreversible as it is, involves a decrease in flow of permeate and hence of productivity. On the other hand, the same phenomenon induces an increase selectivity.

The additional resistive layer that forms on the surface of the membrane is composed of solute, which is captured in this manner by the membrane and can not exit the system with the permeate. Moreover, once the absorption capacity of solute on the membrane, the layer that is formed acts as a real secondary membrane. Both the solvent that the solute must pass through this layer to reach the permeate side. The gel is made just by solute, and therefore the secondary membrane has pore diffusive own order of size of the solute itself: this implies the existence of a very efficient secondary membrane against the solute, with maximized pores with respect to the solvent passage. Unfortunately, all this increases the overall thickness of the membrane and therefore its resistance to flow, from which the drops of productivity.

The behavior of the membranes under fouling can lead in some cases to coefficients of rejections, which we will call apparent, more than 100. In this case, the 6.g equation must be expanded with the condition

$$R_i = 100 \text{ if } R_{the} > 100 \quad (5.h)$$

to keep the physical sense of rejection.

The fouling is the only possible phenomenon capable of significantly reducing the productivity of the module employee. Without the onset of fouling phenomena, it is possible to obtain flow rates of permeate constant over time.

The reversible fouling, due to gelling, is a dynamic phenomenon, which follows the changing operating conditions of the process. As in the previous section, fundamental parameter polarization is the permeate flow  $J_p$  which determines the entity. The geleificazione starts to achievement of certain solute concentrations, global or local they are, on the surface membrane. The layer that is formed is of the dynamic type stationary, with many of solute particles who abandon the gel phase of how many are added over time. With the flow increases permeate, the network of gelled aggregates tends to grow and self-sustaining of the solute particles that can capture more supply. It breaks the dynamic equilibrium of the layer, and eventually reach the solidification conditions: you start the irreversible fouling.

It defines critical flow  $J_c$  the permeate flow maximum obtainable from a membrane module, It will also establish without fouling irreversible.

When operating in conditions below the critical flow it does not undergo any kind of fouling, and you get a permeate flow constant. At critical condition, reversible fouling starts to form. The development of the gelled layer finds its balance, if the operating conditions are not varied, in the critical flow value  $J_c$ . If the operation is pushed over the conditions criticism, began to appear irreversible fouling. It is observed in addition to the flux reduction of permeated even a reduction of the critical flow value  $J_c$  in time. The irreversible fouling leads to a rapid and premature aging of the membranes, and consequently the equilibrium value on which the system settles it will no longer be the same as previously found in critical condition.

From Figure 5.6 it is possible to see how an increase of TMP above a certain  $TMP_c$  critic, for which are obtained permeate flows equal to the value of  $J_c$ , They are completely canceled in time. A higher flow of solvent through the membrane causes an increase in strength convection on solute. The system tries to find a new equilibrium, using the part of the TMP

above the  $TMP_c$  to further compress the gel, thus increasing the thickness and density.

Once past the solidification concentration  $c_s$ , it is produced irreversible fouling. The solvent flow, at this point, is partially blocked and begins to decline: the exercise that the membrane must withstand is relaxed, the irreversible fouling stops and the gelation of Membrane switches to new equilibrium conditions.

Eventually, the system finds new critical conditions which bring. We can see the fouling irreversible as a part of the membrane of self-defense phenomenon: when the exercise required abundantly exceeds its capacity, it reduces the permeate flows drastically for induce an exercise compatible with their productivity limits.

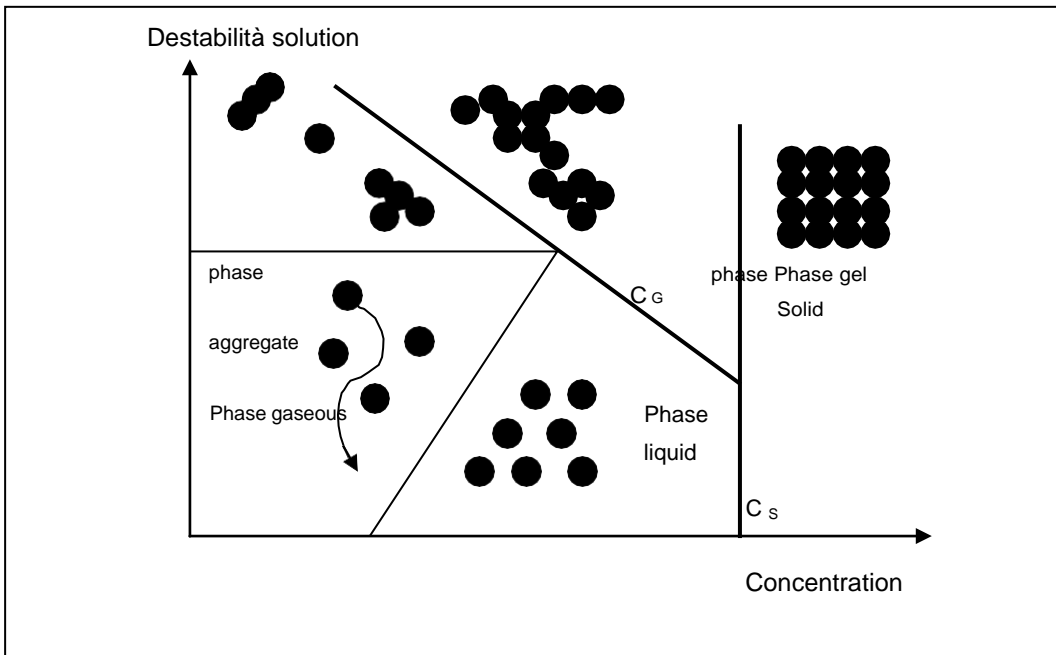
The value of the critical flow depends on many parameters such as temperature, nature and concentration power, the extent of irreversible fouling already present on the membrane, the age and surface characteristics of the membrane itself. larger pollutant particles, increases power flow, the use of membranes with larger pores are some of the measures that lead to an increase in the critical flow value.

All these parameters, many of empirical nature, can not be considered in a single model General mathematician. The determination of the critical flow occurs in an experimental way, and the data They can only be treated with semi-empirical relationships.

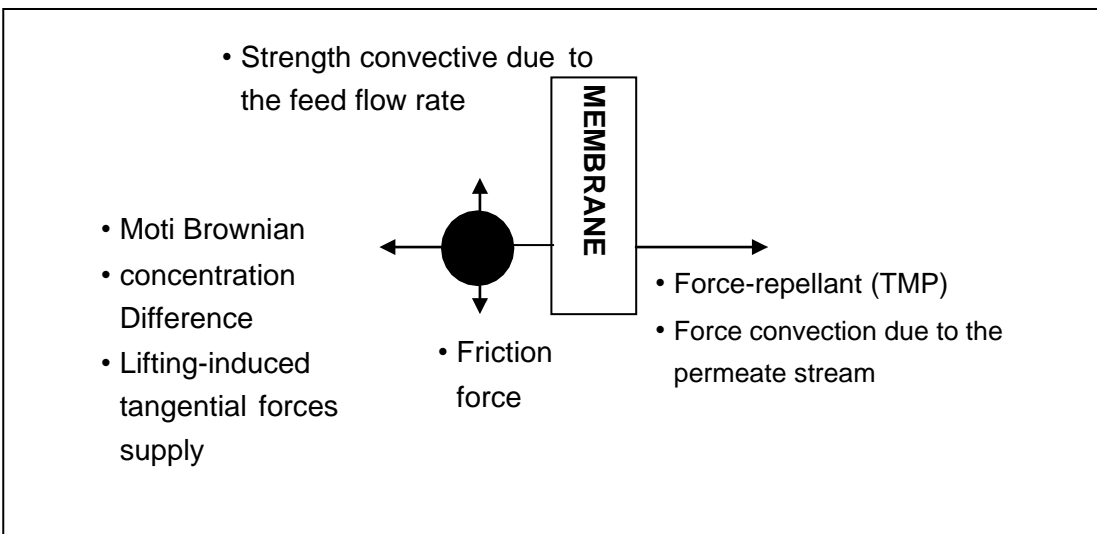
The critical flow theory is nowadays the means most used to study the effects of fouling. Unfortunately it has been noticed that operate in critical conditions for extended periods may form however the irreversible fouling. In fact, one in critical condition we gelled layer saturated, which may exceed locally for a few moments, the concentration of solidification and crystallize on the solid membrane. For this reason, many authors now speak flow sustainable. The sustainable flow  $J_s$ , lower  $J_c$ , It is a permeate flow such that, compatibly with the operating times of separation that you want to get on a particular service for the system under consideration, is as far away from the critical condition. The benefit of designing a system on a sustainable flow value is to get as resulting in a more durable system. This leads to overestimate the surface as much as possible active membrane to be used, consistent with the considerations and technical constraints cost imposed by the service.

The life of membranes is determined both by irreversible fouling that natural aging the material that undergoes over time. A membrane module is declared dead and will be replaced when the critical flow value, or sustainable, falls below acceptable values. In jargon, it is called "short-term fouling" irreversible fouling induced by the operating conditions hypercritical, because it occurs in a sensitive and fast. In contrast, the "long-term fouling" , who mistakenly attaches a fouling phenomenon to aging and wear of the material that makes up the membrane, reduces the flow of permeate in a much slower over time. Some authors have developed relations between the useful life of the membranes and the number of cycles washing carried out. The method is based on the consideration that the number and frequency of washes, the which is subjected the membrane, is the fouling index of the service, and then the likely and irreversible fouling is produced. A greater frequency of washing indicates that the membranes are subjected to greater fouling regime, and as a consequence will increased likelihood of a shorter life.

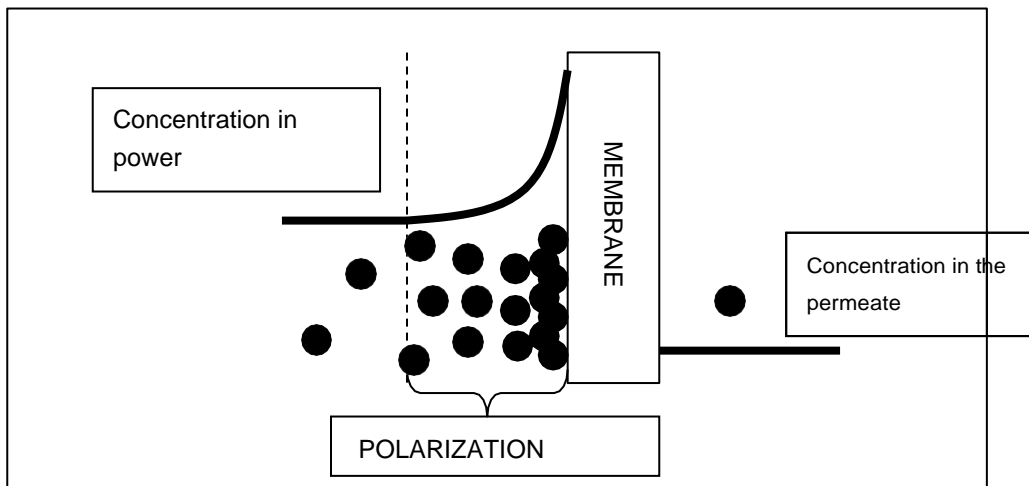
In conclusion, we should never compensate for reduced productivity with pressure increases operational, but with pressure or decreases with the increase of the number of modules committed. The process control plans to control the outgoing flow of permeate equal to value of sustainable flow.



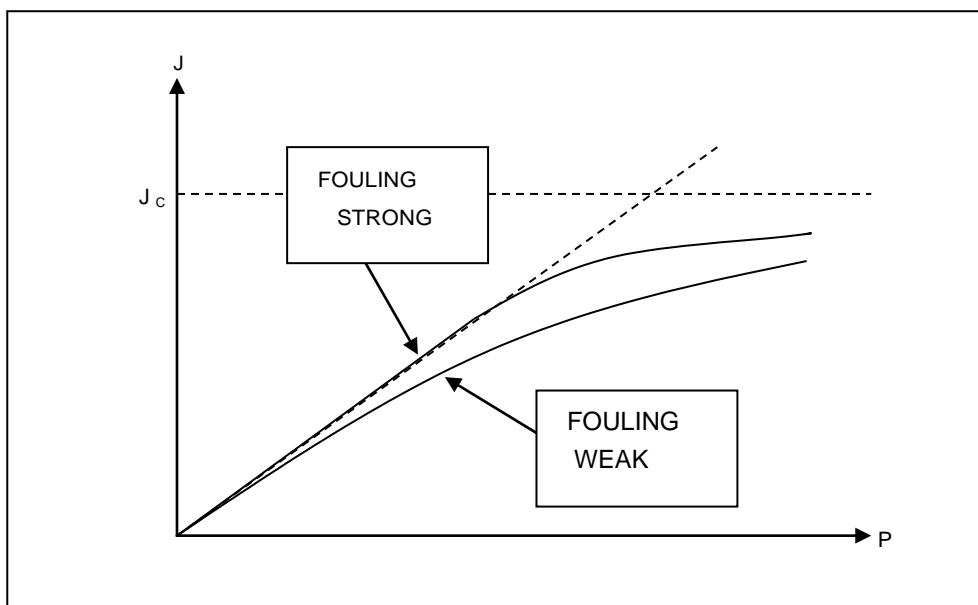
**FIGURE 5.1:** Phase diagram



**FIGURE 5.2:** The forces acting on a particle in the vicinity of the membrane surface.

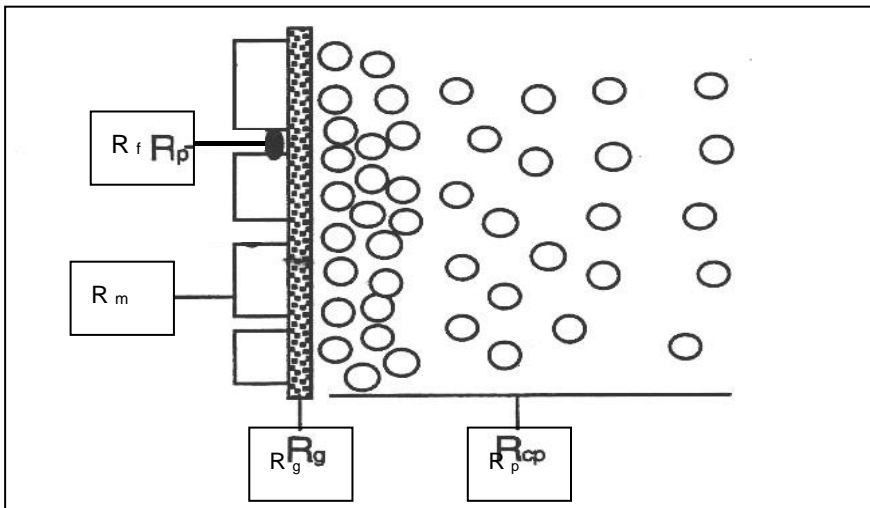


**FIGURE 5.3:** Polarization of the membrane.

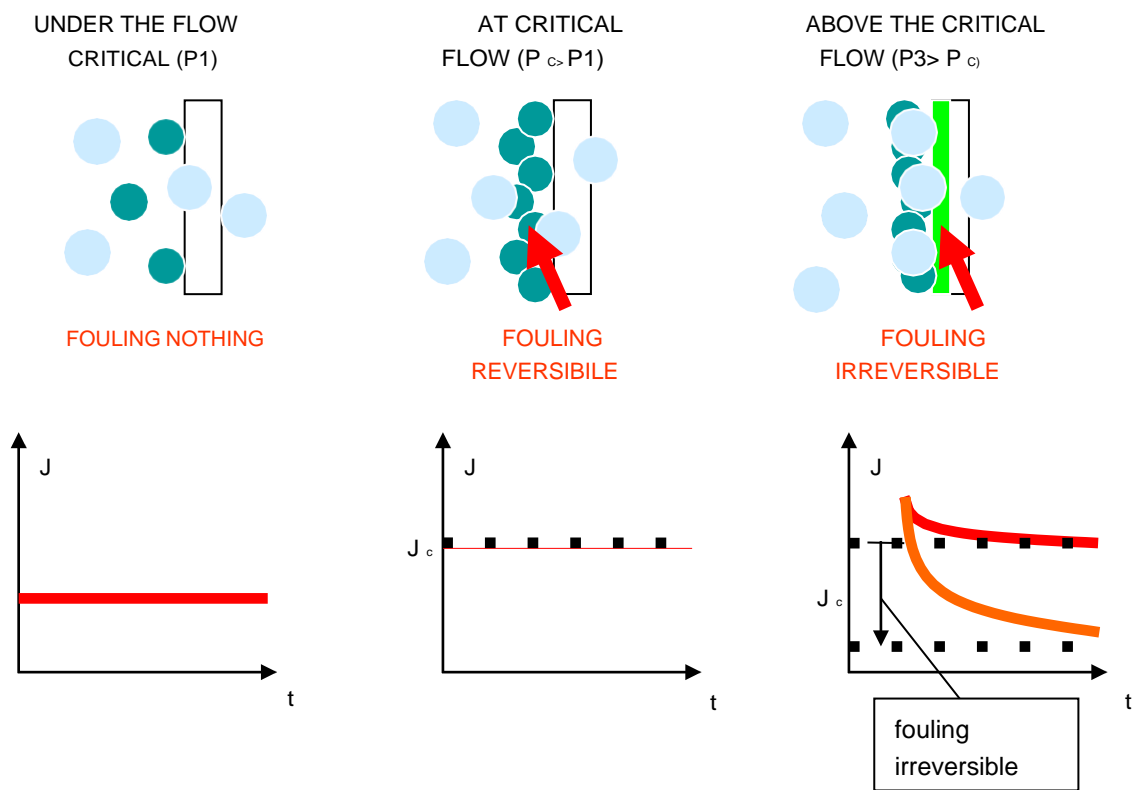


**FIGURE 5.4:** Fouling strong and weak.





**FIGURE 5.5:** Resistances in membrane processes.



**FIGURE 5.6:** The critical flow

## **CHAPTER 6**

### **THE DESIGN OF A SYSTEM MEMBRANE**

The design of a membrane plant requires specific knowledge of the membranes, its performance, and application. The first choice requires if it is appropriate to proceed with a batch process (batch), with or without continuous recycle, semicontinuous. The choice affects performance, the membrane area, the residence time and the complexity of the scheme to be implemented. We need to find the operating conditions between the flow rate of the membrane crossing and pressure.

With the aid of Figure 6.1, the parameters normally known at the design stage are  $c_f$ ,  $pH_f$  (self necessary),  $F_p$  design,  $c_p$  design and therefore  $Y$  (here  $r$ ),  $R$ .  $F$  should be determined, minimum of send to each module, the membrane area  $A_m$  and the operating pressure  $P$ .

Some choices are determined by the supply characteristics (see Table 6.1).

Generally, flows of permeate design are sub-critical flows, amounting to sustainable values, to a determined sub-critical operating pressure  $P$  and at a minimum flow of feed  $F_f$ . On the basis of this flow, the value of  $F_f$  employed, the value of  $P$  and the associated value of  $F_p$  design, it is possible to determine the membrane area  $A_m$ . In this manner, it is possible to obtain the value of the  $Y$  predetermined recovery.

In the case of discontinuous processes, the design is made difficult because of the extreme variability supply, with consequent variation of the critical conditions in time. In this case, sustainable flow should be considered at the end of operation, the most concentrated and operating conditions therefore, more stringent.

All this does not guarantee in any way the achievement of quality of permeate design (rejection  $R$ ), which depends on the polarization (and thus the operating pressure) as well as by the choice of the material that makes up the membrane (membrane type). If it were not possible with the system reach the predetermined purification, be necessary to change the type of membrane, and then repeating the whole design procedure: each of the different membrane model suppliers has for the same power supply and for the same procedural conditions flows of permeate and rejections different, which will be studied on a pilot plant.

## FEASIBILITY STUDY '

The feasibility study opens technical and economic aspects. Narrowing the considerations to aspects technical, it should be placed from the start of the attention to valuations:

- The characterization of the supply current
- The quantification of the membrane separation process performance
- The process scheme to be implemented

An initial study is then made at an experimental level on a pilot plant in the conditions as possible close to those of the industrial plant. Note that the scale factor maximum that can be applied is equal to 10. The aspects to which pay more attention in the phase of definition of the system diagram are in addition to the characteristics of the separation process membrane

- Security problems
- The machinery and auxiliary equipment

The information to be acquired over concern that the recovery rate and the retention of the fouling also in relation to pre-treatment facts.

The parameters of the stream to be treated and their meanings are listed in Table 6.1.

There is no single solution as the case may allow different configurations next performance. The experimental work can be done in laboratory and pilot scale, but Note that only in the latter case you can study fouling. An important aspect to experimentally evaluate is the pretreatment, consisting of filters, flocculation etc., which can sometimes constitute a considerable portion of the total investment

### Estimate the area of the membrane

In the case of discontinuous operation you will find that the ratio between the areas  $A_2$  and from  $A_1$  membrane adopted is directly proportional to the volume treated zone per unit of time, namely:

$$t_2/t_1 = TO_2/TO_1$$

(6.a)

Alternatively the area can be derived from the flow rate of permeate and from the relationship between flow the permeate and the solute concentration in the feed. There is usually a relationship semilogarithmic between the flow and the concentration of the solute. By varying the time the concentration the rejected increases and the flow rate of the permeate is reduced: the area of the membrane must be such as achieve the total volume of the permeate in a reasonable time. In the operation continues You can write the mass balance of the solute of interest and the global one for the area of unitary membrane:

$$J_f = J_p + J_c$$

$$J_f C_f = J_p C_p + J_c C_c \quad (6.b)$$

From the recovery factor of the Y projects is defined for which recovery is known if the rejection is R They can determine from 6.b:

$$J_f C_f = J_f Y (1 - R) C_f + J_f (1 - Y) R C_f \quad (6.c)$$

The area of the membrane will then be equal to

$$A = F_p / (J_f Y) \quad (6.d)$$

to get the flow of permeate project  $F_p$ . Everything for the single-stage

In the process design is of great importance pump. In Figure 6.3 it is indicated the operating range of different pumps type to guide the choice. The centrifugal pump is that mainly used in membrane processes because they cover a wide range of conditions by operating flow rates of 10 m<sup>3</sup> / ha from 20.000 - 30.000 m<sup>3</sup> / h and discharge operations a few meters to 70-80 basis. The main advantages of a centrifugal pump is its simple form. The diagram of Figure 6.3 shows the characteristic curves of a centrifugal pump operating at different speed of rotation. The pre-treatment is also very important: in particular for the reduction of fouling. Sieve recycle and pre-filters are very important in the case of new reverse. In case of aqueous solutions processes can be used to break down by means of coagulants the operation of flocculation or precipitation of colloidal or natural organic material to be deleted. Another important element in the pretreatment is that the pH adjustment in Ro applications is between 4 and 6 to different engines:

- Minimizing the vinegar hydrolysis of cellulose membranes
- For reduction of the carbonate and bicarbonate present in rejected CO<sub>2</sub> thus avoiding the precipitation of the carbonate.

Finally, the washing required to restore the flux and the selectivity of the membrane to the initial values After fouling. Often cleaning done daily, other times can be made 2- 4 times year. The washing is done manually through a precise recipe. First you do a washing with permeate or water, then switch to chemical washing and subsequently washed even with water.

## PLANT PLANS

The batch processes are preferred when both the performance required to process both the current supply are not constant, or when the quantities to be treated are small.

The simplest scheme (Figure 6.4a) is in open-loop recycling, with the current concentrate which returns to the supply tank.

A more complex scheme is that shown in Figure 6.4b. In this case, part of the concentrate is immediate onward feeding, without passing through the reservoir supply. The advantage of this scheme is that it prevents the applicant compression around the concentrated by a single pump, even if the scheme requires two pumps.

In this type of process it assumes a fundamental role as the operating time  $t$ . At constant purification, an operating time  $t$  requires greater membrane surfaces  $A$  minor (see Figure 6.5).

In the case of continuous process, it may be arranged in single or multiple pass. In the first case, the modules are arranged all in parallel. In this case, all the membranes work under the same conditions but will require a larger pump to ensure the flow of power to all modules. In the second case, all the modules are placed in series: the pump must only overcome the pressure drop of the series, providing the volumetric flow of the project necessary for the first module. The disadvantage is that subsequent modules work with concentrated outgoing from the previous modules, and therefore, in the most severe operating conditions.

In Figure 6.6 also shows the pretreatment stage, which is in general (also for processes continuous) vital. The pretreatment decreases the fouling and improves performance.

Some pre-treatment are possible sedimentation, screening, conventional filtration, flocculation, or less selective membrane processes (MF).

As a result, normally they choose cascade layout design, combining the benefits of both basic provisions (see Figure 6.7). The modules are arranged in parallel and in series, where each stage subsequently has a smaller number of modules as in the meantime decreases the extent of supply.

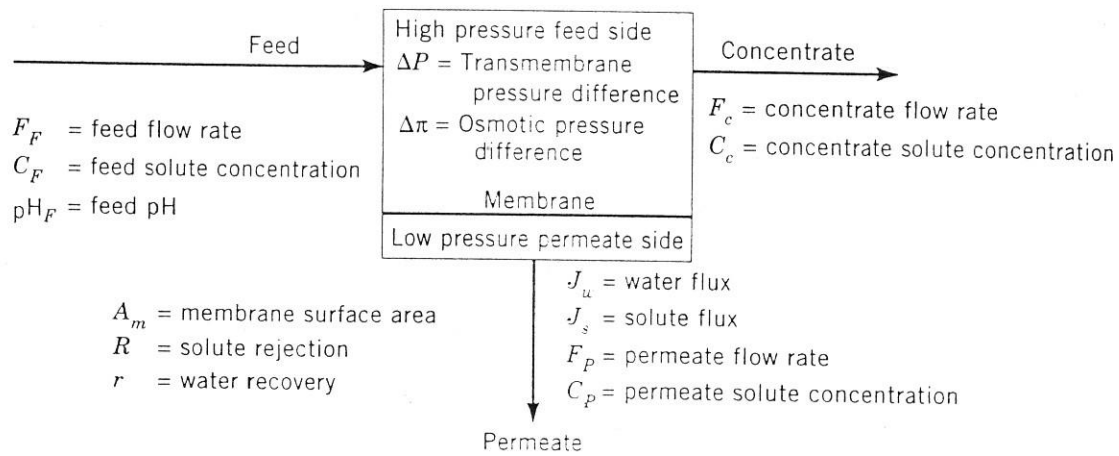
To increase the efficiency of the single-stage separation, you can also be used currents recycling (see Figure 6.8). Normally this requires more pump, but in practice it adds a further separation step to the process.

The recycle are possible both on the concentrate side and the permeate side (Figure 6.9). In the first case, in practice increases the membrane area of the module, while at the time of feeding liquid more residence. In the second case, it helps the separation going to dilute with the solution Purified the starting solution.

Obviously, the speech can also be extended to more stages (Figure 6.10).

Parameters	Significance
Particle size or molecular weight of material to be retained by membrane	Choice of membrane pore size
Settleable solids (size & quantity)	Means of pre-treatment
Shear sensitivity	Module type and pump type
Range of product viscosity	Module type and pump type
Temperature range	Membrane type; heating / cooling requirement; material of construction
pH range	Membrane type; material of construction
Organic solvent content	Membrane type; material of construction

**TABLE 6.1:** Influence on the design choice of some power characteristics.



**FIGURE 6.1:** Operational parameters of membrane processes.

## Effective average flux in a concentration stage

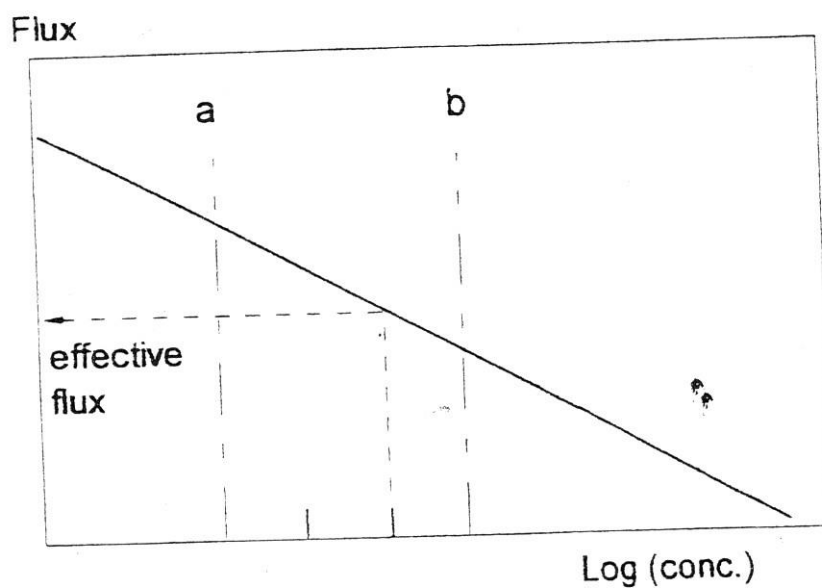


FIGURE 6.2: flow results in relation to the concentration of solutes feeding

## PUMP COVERAGE CHART

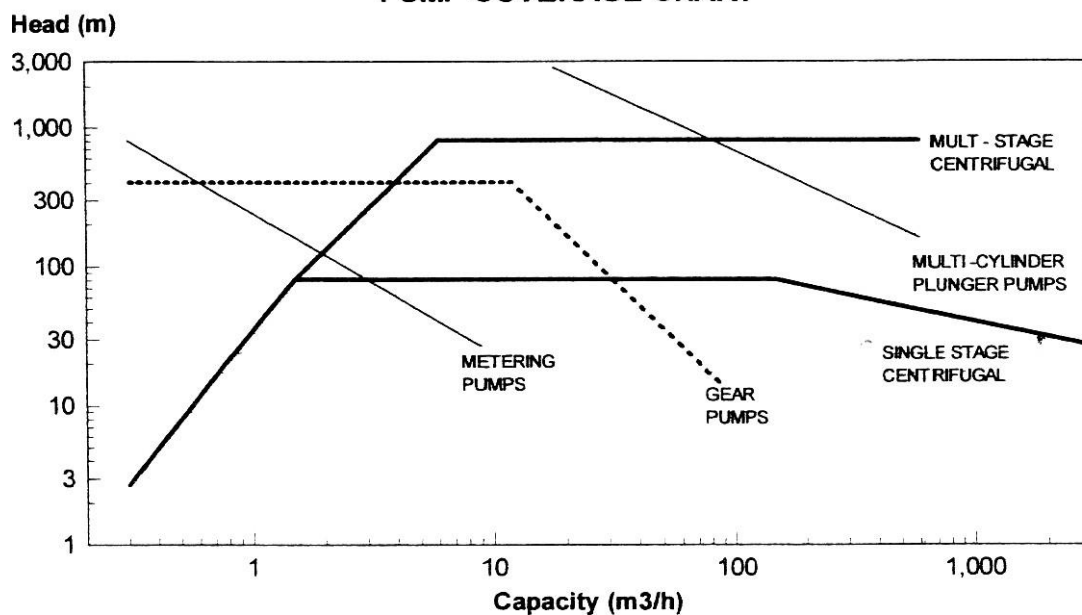


FIGURE 6.3: performance of the various pumps.

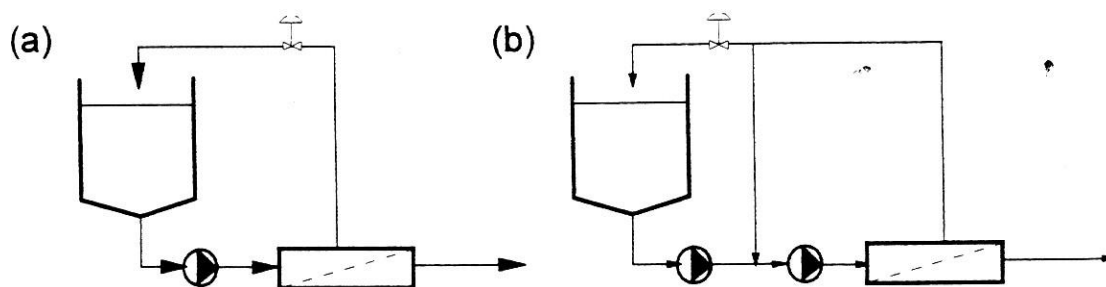
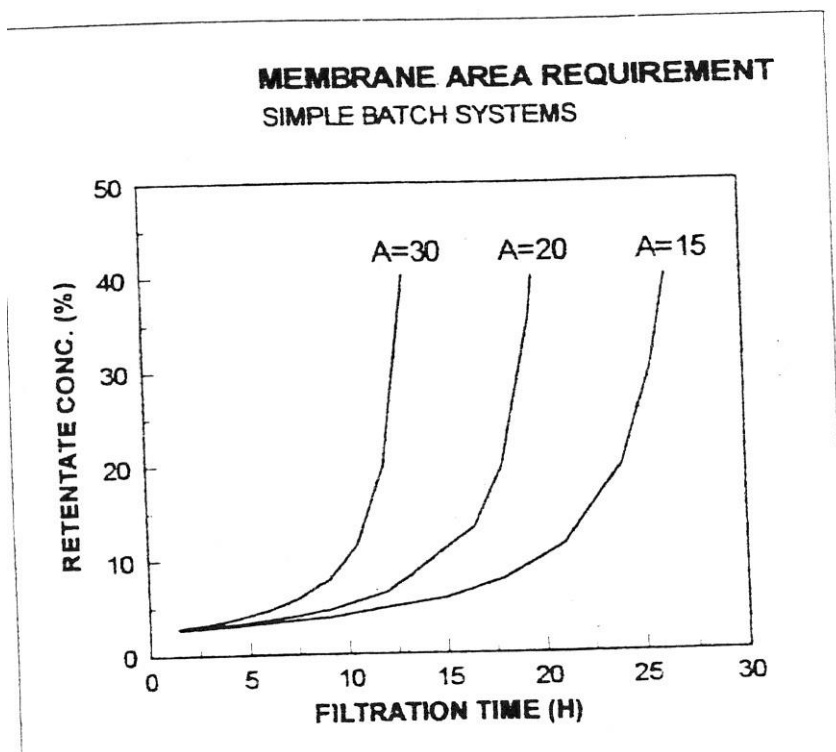
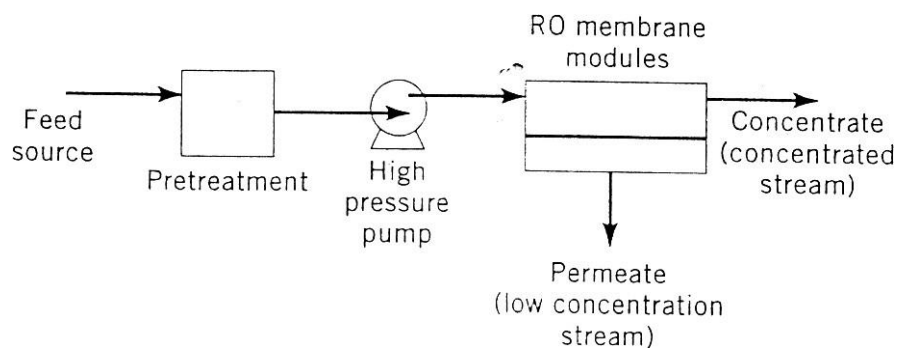


FIGURE 6.4: Batch processes schemes.

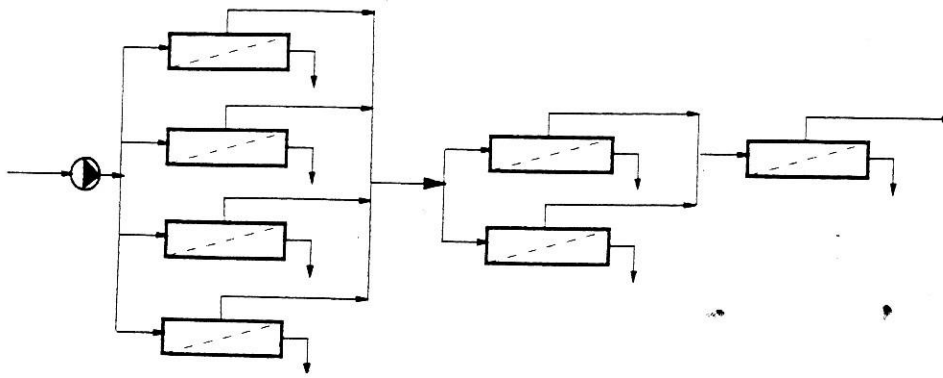




**FIGURE 6.5:** Dependence of the purification and the operating time  $t$  (here H) as a function of membrane  $A$ .



**FIGURE 6.6:** Continuous process.

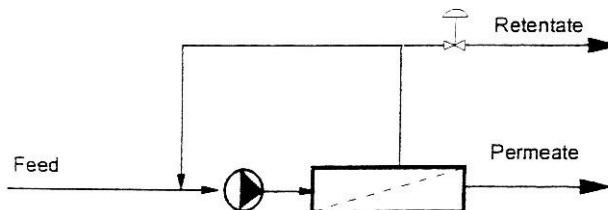


**Figure 8.1-2** Schematic continuous process showing a 3-stage tapered design, popular in reverse osmosis plants.

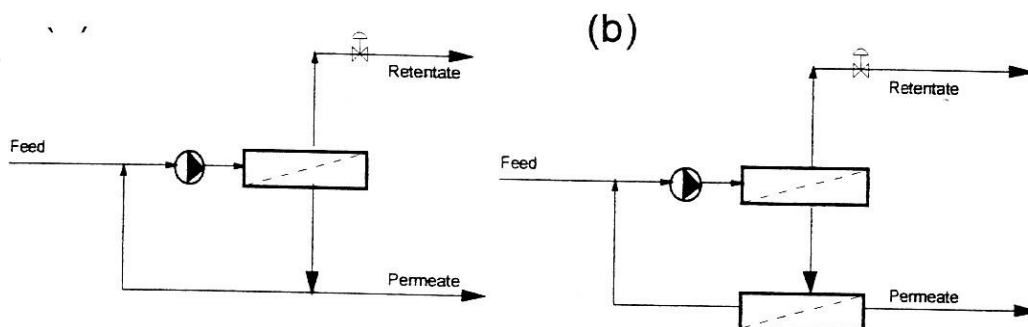
**Table 8.1.1** Number of stages required for target recovery range for reverse osmosis process.

Recovery Target	Number of Stages Required
0 - 50 %	1
50 - 75 %	2
75 - 87.5 %	3
87.5 - 94 %	4

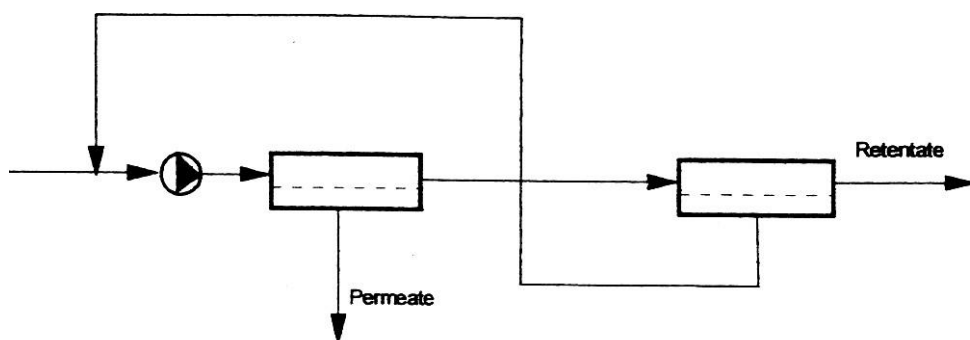
**Figure and Table 6.7:** cascading system diagram.



**FIGURE 6.8:** Diagram with continuous recycling of the concentrate.



**FIGURE 6.9:** Diagram with continuous recycling of the permeate.



**FIGURE 6.10:** continuous two-stage process with recycling.