10. MEMBRANE PROCESSES

10.1. Principles of Membrane Processes

Membrane separation, electrodialysis, reverse osmosis, ultrafiltration and other such processes are playing an increasingly important role in waste water treatment.

A membrane is defined as a phase that acts as a barrier between other phases. It can be a solid, a solvent-swollen gel or even a liquid. The applicability of a membrane for separation depends on differences in its permeability to different compounds.

Table 10.1 gives a survey of membrane separation processes and their principal driving forces, applications and their useful ranges.

Figure 10.1 shows the relation between the membrane permeability and the size of various impurities in waste water. The selection of membrane process is, as seen from this figure, a questionof which impurities are required to be removed from the waste water.

Osmosis is defined as a spontaneous transport of a solvent from a dilute solution to a *concentrated solution across a semi-permeable membrane.* At a certain pressure - the so-called osmotic pressure - equilibrium is reached. **The osmotic pressure** varies with concentration and temperature, and depends on the properties of the solution.

For water, the osmotic pressure is given by:

$$\pi = \frac{n}{V} R T \qquad (10.1)$$

where

n = the number of moles of solute
V = the volume of water
R = the gas constant
T = the absolute temperature

This equation describes an ideal state and is valid only for dilute solutions. For more concentrated solutions the equation must be modified by **the van't Hoff**

factor by using an osmotic pressure coefficient:

$$\pi = \emptyset * \frac{n}{V} R T \tag{10.2}$$

For most electrolytes the osmotic pressure coefficient is less than unity and will usually decrease with increasing concentrations. This means that equation (10.1) is usually conservative and predicts a higher pressure than is observed. If the pressure is increased above the osmotic pressure on the solution side of the membrane, as shown in Fig. 10.2, the flow is reversed. The solvent will then pass from the solution into the solvent. This is the basic concept of reverse osmosis. Reverse osmosis can be compared with filtration, as it also involves the moving of liquid from a mixture by passing it through a filter.

Table 10.1

Membrane separation processes

Process	Driving force	Range (μm) particle size	Function of membrane
Electrodialysis	Electrical potential gradient	< 0.1	Selective to certain ions
Dialysis	Concentration	< 0.1	Selective to solute
Reverse osmosis	Pressure	< 0.05	Selective transport of water and small ions
Ultrafiltration	Pressure	$5 * 10^{-3} - 10$	Selective to molecular size and shape

However, one important difference is that *the osmotic pressure,* which is very small in ordinary filtration, plays an important role in reverse osmosis. Second, a filter cake *with low moisture content cannot* be obtained in reverse osmosis, because the osmotic pressure of the solution increases with the removal of solvents. Third, the filter separates a mixture on the basis of size, whereas reverse osmosis membranes work on the basis of other factors. Reverse osmosis has sometimes also been termed hyper-filtration to be distinguished from ultrafiltration, where dissolved ions and other inorganic molecules are not separated.

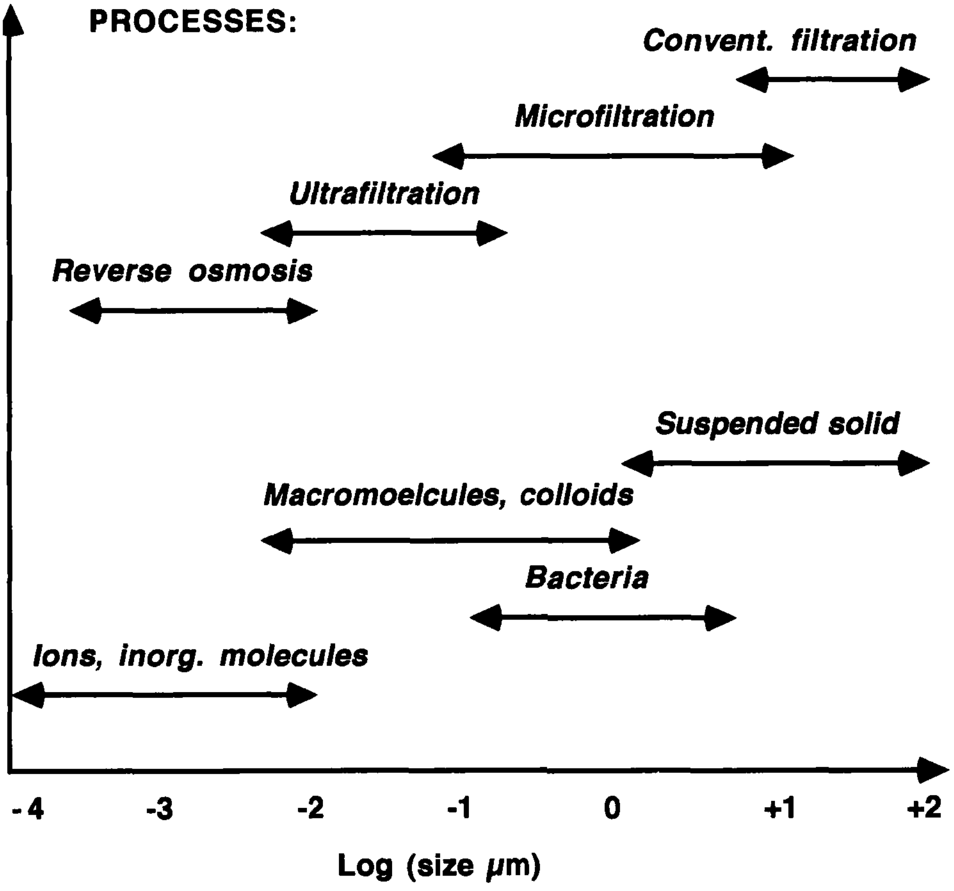

Figure 10.1. Membrane processes and particle size.

The relation between the process and the removable particle size; see Figure 10.1, indicates the possibilities of using membrane processes for nitrogen removal. Proteins can accordingly be removed from waste water and waste products such as whey by application of ultrafiltration. This has found a wide use particularly in the dairy industry. Ammonium and nitrate can be removed at least to a certain extent by use of reverse osmosis. This application has, however, some shortcomings:

1) The osmotic pressure increases to very high levels due to high concentrations of inorganic ions in the reject. This implies that the permeation rate decreases and the required size of the equipment increases. This means high installation costs. The alternative is to accept smaller concentrations of the reject, which, however, increases the problem of reject discharge.
2) It is difficult to avoid a certain clogging of the membranes, although removal of most organics and all suspended matter reduces the problem.
3) The high pressure needed for the process implies high energy costs and therefore high operation costs.

Membrane technology has developed rapidly during the last decades, and it cannot be excluded that reverse osmosis will find a much wider application in the neart future for nitrogen removal, too.

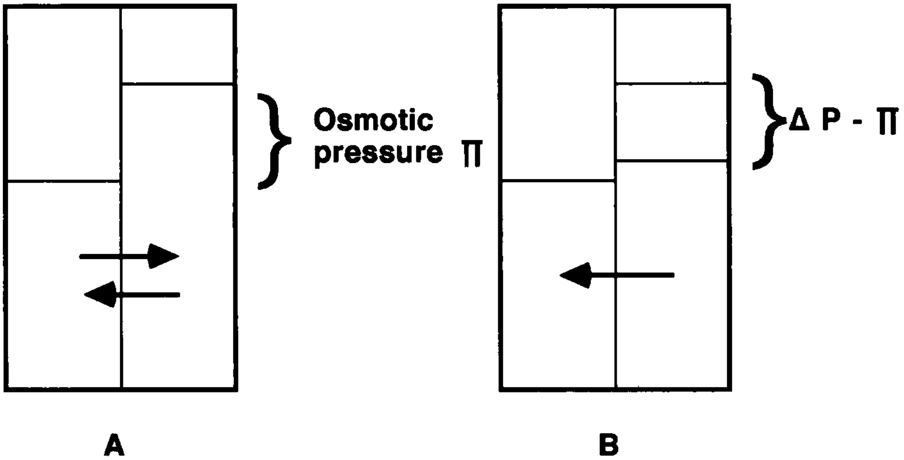

Fig. 10.2. A - illustrates equilibrium. An osmotic pressure appears. B - illustrates the principle of reverse osmosis.

10.2. Process Variables

Reverse osmosis

The permeate flux, F, through a semipermeable membrane is given by:

$$F = \frac{D_s * C_w * V}{R\,T\,d} (\Delta P - \pi) \qquad (10.3)$$

where

D_s = the diffusion coefficient

C_w = the concentration of water

V = the molar volume of water

ΔP = the driving pressure (see Fig. 10.2)

R = the gas constant

d = thickness of membrane

The equation (10.3) indicates that the water flux is inversely proportional to the thickness of the membrane. These terms can be combined with the coefficient of water permeation, W_p, and equation (10.3) reduces to:

$$F = W_p * (\Delta P - \pi) \qquad (10.4)$$

where

$$W_p = \frac{D_s * C_w * V}{R\,T\,d} \qquad (10.5)$$

For the solute flux, F_s, the driving force is almost entirely due to the concentration gradient across the membrane, which leads to the following equation (Clark, 1962):

$$F_s = D_s \frac{dC'_i}{dx} = D_s \frac{\Delta C'_i}{d} \qquad (10.6)$$

where

C'_i = the concentration of species, i, within the membrane

$\Delta C'_i$ = concentration difference measured across the membrane

This equation can be restated in terms of the concentration of the solution, C_i, on either side of the membrane, incorporating the so-called distribution coefficient, K_d, which is a constant for the membranes generally used (Lonsdale et al., 1965):

$$F_s = D_s * K_d * \frac{\Delta C_i}{d} = K_p * \Delta C_i \qquad (10.7)$$

where K_p is termed the coefficient of permeability.

W_p and K_p are both characteristics of the particular membrane type.

As seen from equations (10.4) and (10.7), the water flux depends on the net pressure difference, while the solute flux depends only on the concentration. Therefore, as the feed water pressure increases, water flow through the membranes increases, while the solute flow is approximately constant. Consequently the amount and quality of purified water increase as the net driving pressure is increased, but the quality of the water decreases as the feed water solute concentration increases, with a constant pressure, because of an increase in osmotic pressure. As ever more water is extracted from the waste water, the solute concentration becomes higher and the water flux falls. Figures 10.3 and 10.4 illustrate these relations. The water flux as a function of the water recovery and at a fixed pressure is shown in Fig. 10.3 for two different salinities. The variation of the water quality with recovery is shown in Fig. 10.4. As can be seen, the water quality decreases with increasing feed salinity and increasing recovery. This is the problem touched upon as point 1 on p. 339.

The rejection ratio in reverse osmosis, R, is defined on the basis of the following equation:

$$R = \frac{C_i - C_{pi}}{C_i} \qquad (10.8)$$

where

C_i = the concentration of the species, i, in the concentrated stream (reject)

C_{pi} = the concentration of i in the permeate (product).

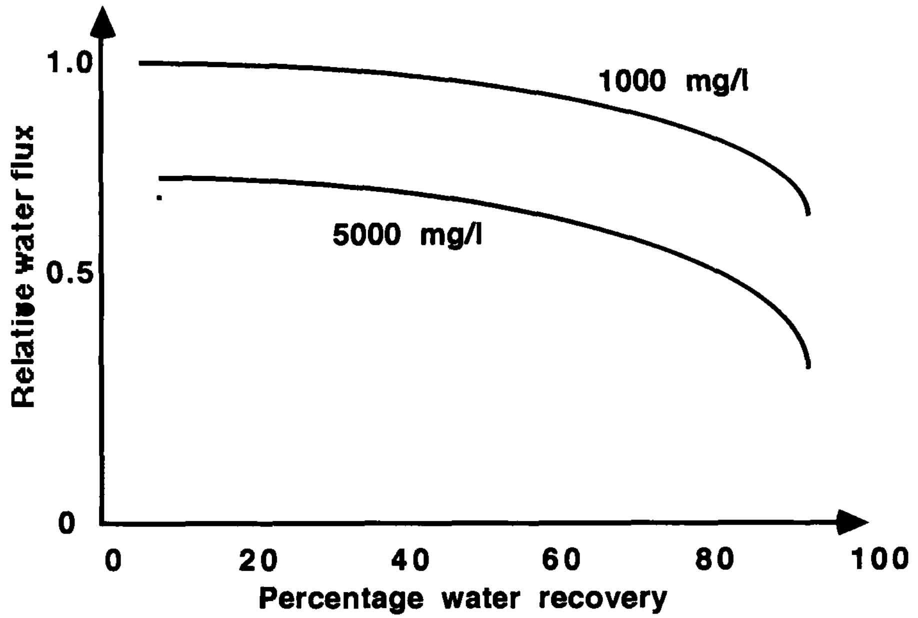

Figure 10.3 Water flux related to water recovery for two concentrations of inorganic components (salts).

The rejection ratio is also expressed by the following equation:

$$R = \left(1 + \frac{K_p * Cw_p}{W_p\,(\Delta P - \pi)} \right)^{-1} \qquad (10.9)$$

where, Cw_p, is the water concentration in the permeate. Notice that $K_p * Cw_p$ and $W_p\ (\Delta P - \pi)$ must be expressed in the same units. As $W_p(\Delta P - \pi) = F$ is often expressed as g or kg / cm_2 or m^2 / sec. Cw_p must be expressed as g / cm^3 or kg / m^3.

The equations given so far are idealized because a good mixing on the brine side has been assumed, so that there is no concentration polarization. However, in reality salt concentrations build up at the membrane surface and a concentration gradient is established.

The increased concentration of the membrane surface raises the local osmotic pressure, so reducing the driving force. Concentration polarization is defined as the ratio of the salt concentration at the membrane surface to the salt concentration in the stream.

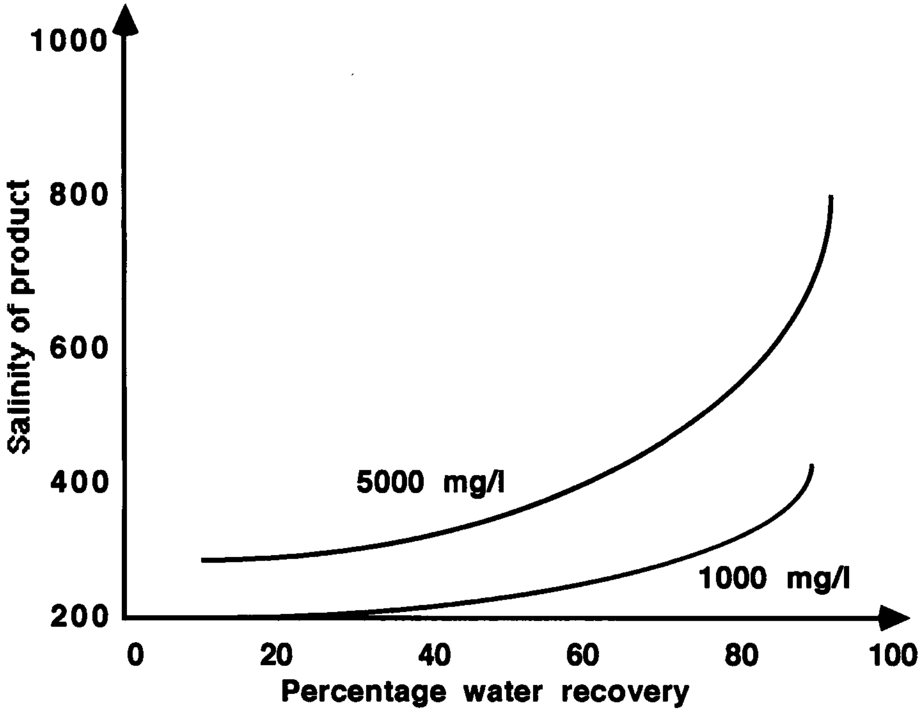

Figure 10.4 Quality of product related to water recovery for two concentrations.

When the concentration adjacent to the membrane surface exceeds a critical value, the flux begins to level off with increasing driving pressure, ΔP. The flux is then controlled by the membrane permeability as well as the concentration polarization. This is illustrated in Fig. 10.5.

The following differential equation describes concentration polarization:

$$\frac{F * C_i}{C_{wc}} - D_s \frac{dC_i}{dx} = K_p * \Delta C_i \qquad (10.10)$$

where C_{wc} is the water concentration in the reject.

If the membrane is impermeable to the solute, it means that $K_p = 0$, and equation (10.10) can be integrated to give:

$$\frac{C_{im}}{C_{ia}} = \exp\left(\frac{F * d}{C_{wc} * D_s}\right) \qquad (10.11)$$

where

C_{im} = the concentration of i in the fluid at the membrane surface

C_{ia} = the average concentration of i in the reject.

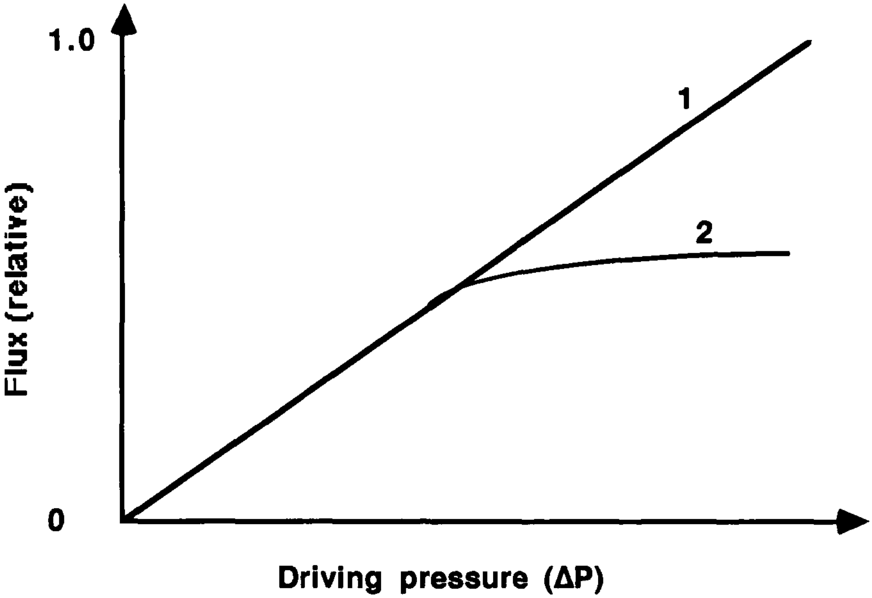

Figure 10.5. Curve 1 illustrates the relation between flux and driving pressure by membrane permeability control, and curve 2 shows the same relation by membrane permeability- and concentration polarization control.

Equation (10.12) indicates the usual relation between flux and concentration of retained substances. The flux decreases, see equation (10.12) with increasing concentration of retained substances:

$$F = k * \ln(C_s / C_i) \qquad (10.12)$$

where

k is an overall mass transfer coefficient

C_s is the concentration of retained species adjacent to the membrane surface

C_i is the concentration of the species, i, in the concentrated stream (reject)

The following description for polarization in turbulent flow has been developed:

$$\frac{C_{im}}{C_{ia}} = 1.333 \exp\left(\frac{2F \cdot Sc^{2/3}}{p \cdot 0.75 \cdot v \cdot f}\right) \qquad (10.13)$$

where

v = the mean velocity

Sc = the Schmidt number (the definition; see Section 7.4)

f = the fanning friction factor

p = the specific gravity of the solution.

The concentration polarization is seen to be a function of the ratio, average product flow rate to average brine velocity, the fanning friction factor and the Schmidt number. Since F/(p*v) is almost proportional to recovery, polarization is favored by high recovery. However, high recovery can be maintained at low concentration polarization by recirculating the brine. The concentration polarization can be reduced by increasing the friction factor, so promoting turbulence.

The concentrations of the ions in the waste water, the required concentrations in reject and effluent are the dominating variables in membrane processes. They determine the relation between flux and pressure according to the equations given above.

However, the temperature and pH play an important role in the durability of membranes. This is illustrated for cellulose acetate membranes in Figure 10.6. Cellulose acetate is not recommended for extreme pH values or high temperatures, but it is widely used due to its moderate costs. At extreme conditions other membranes should be chosen; see Section 10.4. The relationships for all types of membranes between on the one side the durability and on the other side pH and temperature are approximately as illustrated for cellulose acetate in Fig. 10. 6.

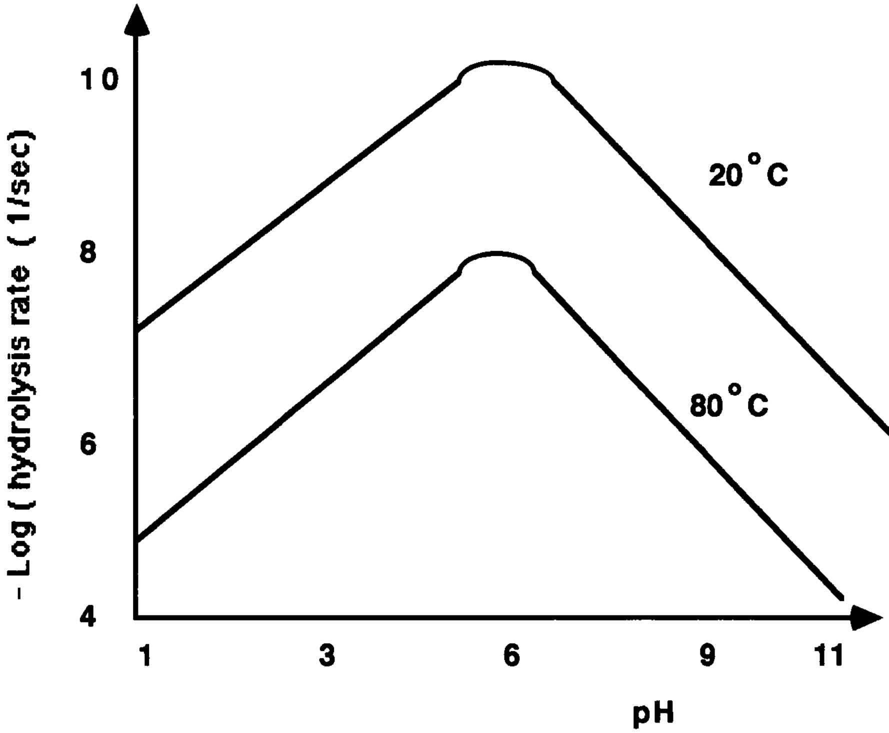

Figure 10.6. Hydrolysis rate of cellulose acetate membrane as function of pH at two different temperatures. Results from Voss et al. (1966).

Ultrafiltration

Both ultrafiltration and reverse osmosis depend on pressure as the driving force and require a membrane that is permeable to some components and impermeable to others.

The difference between the two processes is that, while ultrafiltration is usually used to separate solutes above a molecular weight of 500-2000, which implies a relatively small osmotic pressure, reverse osmosis is used to remove material of low molecular weight, which causes a high osmotic pressure. The polarization is, however, usually greater by ultrafiltration than by reverse osmosis, because the diffusion constant is two or three orders of magnitudes smaller for the macro-molecules than for inorganic ions.

10.3. Design of the Reverse Osmosis Unit

A reverse osmosis plant consists of a series of modules arranged in parallel. The design data include recovery, pressure, brine, flow rates, product water quality and flux maintenance procedure.

To be able to design a reverse osmosis unit one must know the feed water composition, its temperature and osmotic pressure. The capacity requirements of a plant are usually based on a certain reject flow rate at a given temperature or, in the case of waste water treatment, on the feed flow rate.

Based on mass balance for the water as well as the solute, the following equations can be set up:

$$Q_f = Q_r + Q_p \qquad (10.14)$$

$$Q_f * C_{if} = Q_r * C_i + Q_p \bullet C_{ip} \qquad (10.15)$$

where

Q_f = flow rate of feed stream

Q_r = flow rate of reject

Q_p = flow rate of permeate

C_{if} = concentration of i in the feed stream

C_i = conçentration of i in the reject

C_{ip} = concentration of i in the permeate

The mean concentration of i, C_{ia}, on the one side of the membrane is given by:

$$C_{ia} = \frac{Q_r \bullet C_i + Q_f * C_{if}}{C_r + C_f} \qquad (10.16)$$

The water quality in the permeate (product) can be expressed by means of C_{ia} and the average rejection ratio, R_{av}:

$$C_{ip} = C_{ia}(1 - R_{av}) \qquad (10.17)$$

The average salt rejection is given by:

$$R_{av} = 1 - \frac{K_p * C_{wp} \cdot \Delta C_i}{W_p (\Delta P - \pi) C_{if}} \tag{10.18}$$

This equation can be solved most easily by an iteration. If we assume $C_{ip} = 0$, we have:

$$Q_f * C_{if} = Q_r \cdot C_i \tag{10.19}$$

$$C_{ia} = \frac{Q_f * C_{if}}{Q_f * Q_r} = \frac{C_{if}}{2 - R'} \tag{10.20}$$

where

$$R' = \frac{Q_p}{Q_f} \tag{10.21}$$

C_{ip} is then estimated:

$$C_{ip} = \frac{C_{if}}{2 - R'} (1 - R_{av}) \tag{10.22}$$

A better approximation can be obtained by utilizing the value given by equation (10.22) as next C_{ip}-value, etc.

The minimum free energy requirement is determined (Johnson et al., 1966) by means of:

$$\Delta G = -RT \int_0^1 \ln a_w * dn_w \tag{10.23}$$

where

a_w = the chemical activity of water

n_w = number of moles of water recovered

a_w can be calculated from:

$$\ln a_w = \sum \varphi * C_i / 55.5 \qquad (10.24)$$

where φ is a coefficient.

10.4. Reverse osmosis system

In constructing a system for reverse osmosis many problems have to be solved:

1. The system must be designed to give a high liquid flux reducing the concentration potential.
2. The packaging density must be high to reduce pressure vessel cost.
3. Membrane replacement costs must be minimized.
4. The usually fragile membranes must be supported as they have to sustain a pressure of 20-100 atm.

Table 10.2

Comparison of the various techniques

Modul concept	Packing density (m2/m3)	Useful pH range	Ease of cleaning	NaCl rejection	Water flux at 40 atm. (m3/m2/day)
Plate and frame	450	2-8	fair	very good	0.5
Large tubes	150	2-8	very good	very good	0.5
Spiral	750	2-8	good	very good	0.5
Hollow fine fibers	$7.5\text{-}15^{*}\ 10^{3}$	0-12+)	fair	good/fair	0.05-0.2

+) Polyamide

Four different system designs have been developed to meet the solution to problem 4. These are the plate and frame technique, large tube technique, spiral wound technique and the hollow fine fiber technique.

The various techniques are compared in Table 10.2. The most widely used membrane is the cellulose acetate membrane made by the Loeb-Sourirajan technique. This membrane is asymmetrical and consists of a thin dense skin of approximately 0.2 μ on an approximately 100 μ thick porous support.

Polyamide membranes have also been developed. They are considerably more resistant to high pH-values, but give a smaller flux. During the last two decades there has been an intense research activity in the development of membranes, resulting in several new types. Cellulose acetate-butyrate resin, cellulose acetate-methacrylate, polyacryl-acid and cellulose nitrate-acetate, are among the recently developed membrane materials, which are more resistant to pH and temperature, but do not reduce the initial fluxes. Several natural materials could also be of use as membranes and extensive laboratory investigations may hold promise for the application of such natural membranes soon (Kraus et al., 1967).

Table 10.3 gives the characteristics of some widely used types of membranes.

Table 10.3.

Characteristics of membrane material

Material	**pH-stability**	**Chlorine resistance**	**Biological resistance**	**Temp. range°C**	**% Ion separation**
Polyamide	4-11	not good	good	< 35	>90
Cellulose acetate	2-8	good	not good	< 30	90
Cell. tri-acetate	4-8	fair	fair	< 30	90
Polyacrylic acid	2-11	fair	good	< 40	>90
Cell. acetate-butyrate	2-10	good	fair	< 35	90
Combined membranes	2-12	fair	good	< 50	>90

As mentioned in Section 10.1 it cannot be excluded that new and better membranes will be developed in the coming decade, which will make the use of reverse osmosis economically attractive for removal of inorganic nitrogen ions, i.e., ammonium and nitrate. This will have particular interest, where production of drinking water quality from municipal waste water will be needed due to problems of water shortage.

10.5. Application of Reverse Osmosis and Ultrafiltration

EPA has for several years performed experiments to determine the feasibility of membrane techniques in treatment of municipal waste water. The results can be summarized in the following 5 points (EPA, 1969, Feige and Smith, 1974 and Bilstad, 1989):

1. The flux decreased over a period of 20 days and was then stabilized.
2. The quality of the influent was important for the flux. Chemical precipitation seems to be an appropriate pretreatment to use in this context.
3. It is technically feasible to separate nitrogen and other compounds from the waste water.
4. The major problems are concerned with the material-technology. These problems may be solved in the very near future.
5. It is possible to remove impurities on the membranes chemically to obtain the same flux as for new membranes.

The results obtained by EPA at the Pomona waste water treatment plant are shown in Table 10.4. The shown results were obtained with the spiral technique used at a pressure of 31 kg / cm^2. The waste water was pretreated on activated carbon.

Similar experiments have been performed in Tokyo, using different types of membrane processes. The aim was to find suitable methods to recover waste water. A final report from these experiments is expected soon, but the provisional results have indicated that it is possible to obtain a certain removal of nitrogen compounds by ultrafiltration.

The widest application of membrane processes for removal of nitrogen compounds from waste water or waste has been the use of ultrafiltration to remove water from whey (rich in proteins) and municipal sludge. Whey was previously used as pig feed, but due to the high dilution, the transportation to the farms became uneconomical. It is, however, possible to obtain protein concentrations 4-6 times higher by ultrafiltration, which reduces the transportation cost correspondingly and makes it again profitable to utilize whey as pig feed. The discharge of nitrogenous material by dairies may thereby be reduced correspondingly.

As seen from this review on the application of membrane processes for the removal of nitrogenous material, the present use is limited, but many waste water engineers and scientists in the field of membrane processes expect a rapid growth in the use of these technologies in the very near future. It seems therefore appropriate to include the presentation of membrane processes in a review of nitrogen removal techniques.

Table 10.4.

Results obtained by reverse osmosis after pretreatment of municipal waste water by biological treatment and activated carbon adsorption. 75% of the water was recovered by the process.

Parameter	**Influent**	**Effluent**	**% separation**
COD mg/l	8.7	1.0	88.5
Ammonium-N	10.1	1.1	89.2
Phosphate-P	10.9	0.2	98. 4
TDS	750	59	92.1