Membranes and Membrane Separation Processes, 2. Design and Operation

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In this chapter, classical membrane separation processes are treated as unit operations. Various process designs and operation concepts are discussed. For other applications of membrane separation processes in ion exchange and electrochemical synthesis see → Ion Exchangers, Section 12.1.10 → Fuel Cells, Sectiom 3.1.2 → Chlorine, Chapter 4 [24]. Facilitated-transport and membrane reactors are still in an early state of development and so far used mainly on a laboratory scale. The same is true for membrane distillation and membrane contactors.

1. Ultrafiltration, Microfiltration, and Reverse Osmosis

Microfiltration, ultrafiltration, and reverse osmosis have many chemical engineering aspects and process design features in common. In all three processes a hydrostatic pressure is utilized as driving force to transport certain components through a membrane which shows different permeability for different components. As a result a feed solution is converted into a filtrate and a retentate. The filtrate contains all components that have permeated the membrane, and the retentate contains the components that are retained or rejected by the membrane. The design of a microfiltration, ultrafiltration, or reverse osmosis process is illustrated in Figure 1.

The performance of a membrane in a pressure-driven separation process is determined by its filtration rate, the membrane flux, and by the membrane separation properties. Membrane flux and separation properties are a function of membrane permeability for the different components of the solution and the applied hydrostatic pressure. But they are also determined by process and systems design.

1.1. Recovery Rate, Membrane Rejection, Retentate and Filtrate Concentrations

The separation capability of a membrane in reverse osmosis or ultra- and microfiltration can

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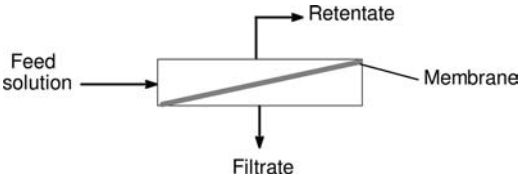

Figure 1. Process scheme of ultrafiltration, microfiltration, and reverse osmosis

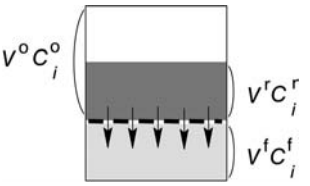

Figure 2. Schematic illustrating a batch filtration with complete mixing of filtrate and retentate

be expressed in terms of *membrane rejection* which describes the "true" rejection of a membrane. The true rejection of the membrane is given by:

$$R = \left(1 - \frac{C_i^f}{C_i^r}\right) \tag{1}$$

where R is the rejection of the membrane for a given component i at a defined hydrostatic pressure and feed solution concentration, and C_i^f and C_i^r are the concentrations of rejected components at a given point at the surface of the membrane facing the filtrate and at the surface facing the retentate, respectively. At a given temperature and pressure the rejection depends only on the membrane properties.

In many practical applications it is more convenient to express the rejection in reference to the feed solution:

$$R_0 = \left(1 - \frac{C_i^f}{C_i^o}\right) \tag{2}$$

where R_0 is the rejection in reference to the feed entering a filtration device and to the filtrate leaving the device after a certain amount of the feed has been recovered as filtrate.

Thus, the rejection in reference to the feed is a function of the recovery rate, which is given by the ratio of the filtrate to the feed volume.

$$\Delta = \frac{V^f}{V^o} \tag{3}$$

where Δ is the recovery rate and V^f and V^o are volumes of the filtrate and the feed solution.

Since in a practical application the concentration in the retentate is limited by factors such as osmotic pressure and viscosity, the solvent of the feed solution can not be completely recovered as filtrate. The recovery rate has a value between 0 and 1.

The concentrations in the retentate and the filtrate are not only determined by true membrane rejection R, but they are also a function of the recovery rate and of the operational parameters such as cocurrent or countercurrent flow of the concentrate and permeate solutions in the membrane device. For a simple batch-type filtration with complete mixing of the retentate and filtrate, as illustrated in Figure 2, the membrane flux is identical over the entire membrane area, and the relation between the concentration of retentate, filtrate, and feed solutions is given by a mass balance:

$$V^o C_i^o = V^r C_i^r + V^f C_i^f \tag{4}$$

where C_i^o, C_i^r, and C_i^f are the concentrations in the feed solution, in the retentate, and in the filtrate.

If concentration polarization effects are neglected the true membrane rejection can be calculated according to Equation (1) by assuming infinitesimal volume change, that is, the recovery rate approaches 0.

The concentration of a component in the retentate and filtrate at a given recovery rate is obtained from the mass balance by integration over the recovery rate:

$$C_i^r = C_i^o (1-\Delta)^{-R} \tag{5}$$

The concentration in the filtrate is directly proportional to that in the retentate. Thus, for a given recovery rate, the filtrate concentration at any given time is found by introducing Equation (1) into Equation (5):

$$C_i^f = C_i^o (1-R)(1-\Delta)^{-R} \tag{6}$$

The filtrate concentration expressed in Equation (6) is the concentration corresponding to a given recovery rate, that is, during an infinitely small time interval. For most practical applications, however, the filtrate concentration obtained during an infinitely small time interval and at a

certain recovery rate is of less interest than the *mixing cup concentration* [2], which is obtained when the entire filtrate up to a given recovery rate is collected and mixed. The mixing cup filtrate concentration $\bar{C}_i$ f can be calculated by integration of Equation (5):

$$\bar{C}_i \mathrm{f} = \frac{C_i^{\mathrm{o}}}{\Delta}[1-(1-\Delta)^{1-R}] \tag{7}$$

The mixing cup concentration is always lower than the concentration obtained during an infinitely short time period at a certain recovery rate. Figure 3 shows the retentate, filtrate, and mixing cup concentrations as a function of recovery rate for three different membrane rejection coefficients ($R = 0.99$, 0.9, 0.8, and 0.5).

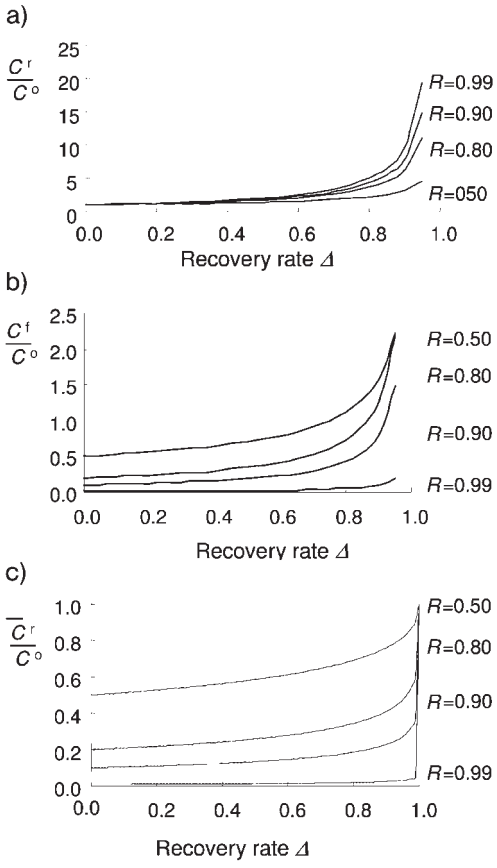

Figure 3. Ratios of a) the retentate to feed solution concentration, b) the filtrate to feed solution concentration, and c) the mixing cup filtrate to feed solution concentration as a function of the recovery rate calculated for different membrane retentions

Figure 3 shows that the retentate concentration strongly depends on the recovery rate and reaches high values for membranes with high retention properties. The concentration in the filtrate also depends on the recovery rate and reaches high values for membranes with low retention properties. The mixing cup filtrate concentration increases less strongly with recovery rate, especially for membranes with high retention properties, and approaches its maximum value of 1 at a recovery rate of 1.

In membrane evaluation or characterization tests, the rejection R of a membrane can be calculated from two easily measurable values: the mixing cup filtrate concentration $\bar{C}_i$ f and feed concentration C_i^{o}.

$$R = 1-\frac{\ln\left(1-\frac{\bar{C}_i \mathrm{f}\Delta}{C_i^{\mathrm{o}}}\right)}{\ln(1-\Delta)} \tag{8}$$

The significance of the mixing cup and maximum retentate concentrations can be illustrated in practical examples. For instance, in the production of potable water from seawater or brackish water, the concentration of total dissolved salts in the filtrates should not exceed 500 mg/L. This concentration is the mixing cup filtrate concentration. For given membrane and feed solution properties it is a function of the recovery rate and can be calculated by Equation (7).

If the feed solution contains a solute with limited solubility such as $CaSO_4$ or $CaCO_3$, the maximum recovery rate is determined by the maximum retentate concentration achievable without solute precipitation. The maximum recovery rate for given membrane and feed solution properties can be calculated by Equation (5).

1.2. Solute Loss in Filtration

In a membrane filtration process, the "product" may be either the filtrate, for example, as in the production of ultrapure water, or the retentate, for example, as in the concentration of proteins from whey. For membranes that are not strictly semipermeable some solute will permeate the membrane with the filtrate. This may affect the quality of the filtrate or lead to product losses.

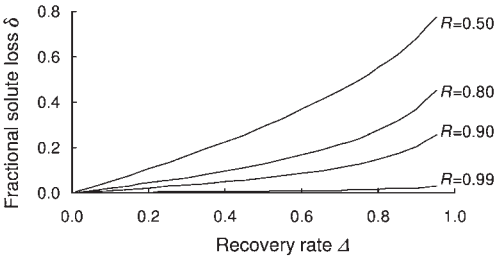

Figure 4. Fractional solute loss in membrane filtration calculated as a function of the recovery rate for different membrane retentions

The *fractional solute loss* δ of a component i is usually expressed by the amount of solute lost with the filtrate divided by the total amount of solute in the feed solution:

$$\delta = \frac{V^{f} C_i f}{V^{o} C_i^{o}} = 1-(1-\Delta)^{1-R} \tag{9}$$

where V^f and V^o are the volumes of the filtrate and the initial feed solution, $\bar{C_i}$ f is the mixing cup filtrate concentration, C_i^o the initial feed solution concentration, Δ the recovery rate, and R the membrane rejection.

Product loss may be significant even with membranes that have a relatively high solute rejection when high retentate concentrations are desired, as illustrated in Figure 4.

1.3. Effect of Osmotic Pressure on the Filtration Rate

The main difference between reverse osmosis and ultra- or microfiltration is the size or molecular mass of the solutes separated from a solution. In reverse osmosis, low molecular mass components are separated from a solvent. A solution of low molecular mass components can have a significant osmotic pressure that must be overcome by the hydrostatic pressure applied as driving force for the separation. The osmotic pressure is always negligibly low in microfiltration. In ultrafiltration of macromolecular solutions it may have an effect on the filtration rate. In reverse osmosis of low molecular components such as salts the osmotic pressure plays a very important role. It often is the limiting parameter for the maximum concentration that can be achieved in the retentate.

The osmotic phenomenon and the osmotic pressure of a solution is discussed in → Membrane Separation Processes, 1. Principles, Section 2.6.1. The osmotic pressure of a solution is proportional to its solute concentration and given by:

$$\pi = RT \sum_i g_i C_i \tag{10}$$

where R is the gas constant, T the absolute temperature, and g the osmotic coefficient, which is a correction factor for the nonideal behavior of a solution, C_i the concentration of a component i, which in a dissociated salt refers to individual particles (i.e. cations and anions).

The membrane flux rate is determined by the effective pressure, which is given by the difference between applied pressure and osmotic pressure. Since the osmotic pressure increases with increasing solution concentration and thus with increasing recovery rate, the membrane flux decreases with increasing recovery rate. In microfiltration and to a large extent also in ultrafiltration the osmotic pressure is negligibly low compared to the applied pressure because of the high molecular weight of the retained components. Therefore, the filtration flux will be independent of the feed or retentate concentration. This, however, is not the case in reverse osmosis. Here, the osmotic pressure is significant for even modestly concentrated solutions and increases with increasing recovery rate. In many applications of reverse osmosis the recovery rate is limited by the osmotic pressure.

1.4. Process Operating Mode

In the practical application of filtration processes three modes of operation are used (Figure 5).

In the batch process depicted in Figure 5a a given feed volume is placed in a pressure vessel. Under a hydrostatic pressure certain components, mainly solvents, permeate the membrane and are collected as filtrate. The components retained by the membrane are concentrated. When a certain concentration in the retentate is achieved the process is terminated.

In the continuous process depicted in Figure 5b the feed solution is continuously fed into the filtration device, which generally consists of a membrane-lined channel or tube.

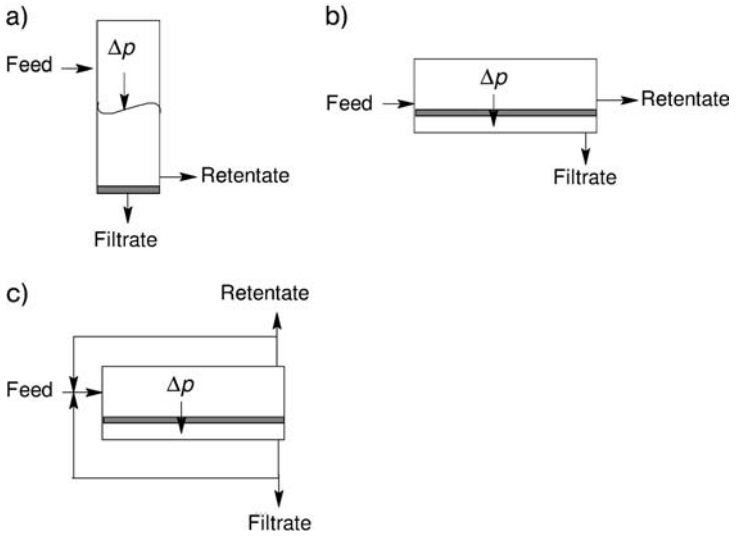

Figure 5. Schematic illustrating different operation modes of filtration processes: a) batch process, b) continuous process, and c) feed-and-bleed process

Under a hydrostatic pressure certain components permeate the membrane and are collected as filtrate, which leaves the device through an outlet port. The retained components are concentrated during passage through the device and leave at the end of the process as the retentate. Depending on the flow velocity of the feed solution, the geometry of the device, and the filtration rate a certain recovery rate is achieved. If the recovery rate achieved in one process pass is not satisfactory a higher recovery rate can be obtained by applying a so-called feed-and-bleed operating mode. In this case part of the retentate is recycled to the device inlet and mixed with the feed solution, as shown in Figure 5c. Depending on the retentate recycling ratio, different recovery rates can be achieved. If a component is not completely retained by the membrane its concentration is proportional to the retentate concentration and thus increases with increasing recovery rate. If the concentration of partly retained components in the filtrate exceeds the desired maximum value in the given process path length part of the filtrate may be recycled to the feed inlet. By adjusting the ratio of the filtrate recycled to the feed to the overall filtrate the concentration in the filtrate can be kept to a desired value.

1.5. Diafiltration Operating Mode

A variation of the ultrafiltration process, generally referred to as diafiltration [3], is often used when more complete separation of micro- and macrosolutes is required. Diafiltration is used, for instance, to remove salts from a mixture with proteins or other macromolecular components. In this application it competes directly with dialysis. The principle of diafiltration is illustrated in Figure 6.

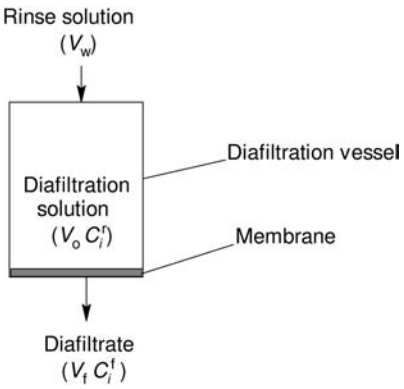

Figure 6. Schematic illustrating the diafiltration operating mode

The diafiltration membrane should retain macromolecular components, but should be permeable to microsolutes. If filtrate removed from the cell is replaced by pure solvent, the low molecular mass constituents are gradually washed out of the feed mixture. If the volume of the original solution is kept constant, the concentration in the diafiltration vessel can be calculated as a function of the membrane retention and the volume of diafiltration rinse solution (i.e., the pure solvent replacing the filtrate volume) by a mass balance which is:

$$\frac{V_f C_i^f}{dt} = -V_o \frac{d C_i^r}{d t} \tag{11}$$

By introducing $V_f = V_w$ and $C_i^f = (1-R)C_i^r$ into Equation (11) and integrating over a certain time period the concentration in the diafiltration vessel can be expressed by:

$$C_i^{rt} = C_i^{ro} \exp -(1-R)\frac{V_w}{V_o} \tag{12}$$

where C_i^f and C_i^r are the concentrations of component i in the filtrate and in the diafiltration vessel, C_i^{rt} and C_i^{ro} the concentrations in the diafiltration vessel at time t and at the beginning of filtration, V_o is the volume of the diafiltration vessel, V_f and V_w are the volumes of the filtrate and the rinse solution added during time t, and R is the rejection of the membrane for the component under consideration.

If the component is completely retained by the membrane (i.e., $R = 1$), the concentration in the batch cell remains constant. If the membrane is completely permeable to the component (i.e., $R = 0$), the concentration in the reactor decreases according to the exponential function of Equation (12). The "rinse-out" effect in diafiltration is illustrated in Figure 7a, which shows the reduced concentration in the diafiltration process as a function of the ratio of the rinse water volume to diafiltration vessel volume calculated for different membrane rejections.

If the macromolecular constituents are only partially rejected by the membrane, a substantial loss of product occurs. If complete removal of the low molecular mass components without substantial loss of macromolecular material is desired, rejection of the membrane should be close to zero for the component low in molecular mass and close to one for the macromolecular material.

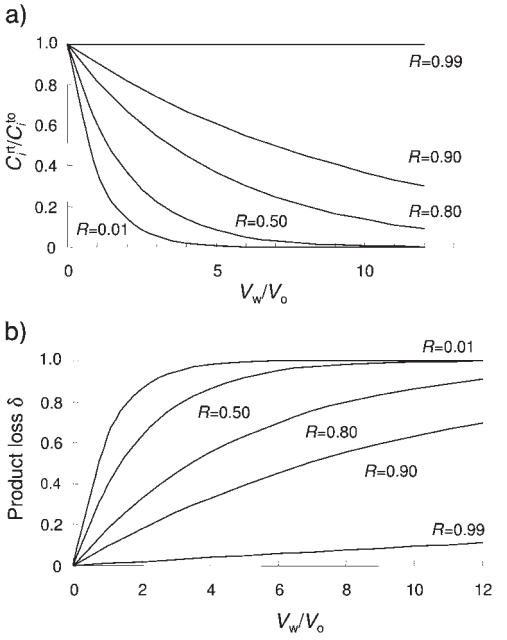

Figure 7. a) Reduced retentate concentration in diafiltration as a function of the ratio of rinse water volume to diafiltration vessel volume calculated for various membrane retentions, and b) fractional product loss in diafiltration as a function of the rinse water volume calculated for different membrane retentions

As in ultrafiltration, product losses may be significant, for example, if the membrane does not reject the macromolecules completely in desalting a macromolecular solution. The fractional product loss δ is then given by

$$\delta = \frac{V^f \bar{C}_i^f}{V^o C_i^o} = 1 - \exp -(1-R)\frac{V_w}{V_o} \tag{13}$$

where V is the volume, R the membrane rejection, $\bar{C}_i$ f the mixing cup concentration, C the concentration, superscripts o and f refer to the initial feed solution and the filtrate, and subscripts o and w to the original volume of the feed and the volume of the wash solution.

In Figure 7b the fractional product loss is shown as a function of the ratio of wash solution volume V_w to feed solution volume V_o for membranes with different rejection characteristics. The concentration of a low molecular mass solute is reduced to less than 1 % of its original value by a wash solution volume five times that of the feed solution volume when the membrane passes the solute unhindered (i.e., R approaching 0), as shown in Figure 7. If the solute is partially

rejected by the membrane, correspondingly more wash solution is required to reduce the concentration of the low molecular mass solute below a certain value. On the other hand, when the membrane rejects the macrosolute completely (i.e., R approaching 1) no product is lost, but partial rejection leads to significant product loss, as shown in Figure 7b.

2. Gas Separation

In gas separation, a feed stream enters a membrane device as indicated in Figure 8. Under the driving force of a hydrostatic pressure difference, some components permeate the membrane while others are retained, and a feed stream is split into a permeate and a retentate.

The different flow streams illustrated in Figure 8 are related with each other by the mass balance:

$$Q^{\mathrm{f}} X_j^{\mathrm{f}} = Q^{\mathrm{p}} X_j^{\mathrm{p}} + Q^{\mathrm{r}} X_j^{\mathrm{r}} \tag{14}$$

where Q is the flow stream, X the molar fraction of the component j, superscripts f, p, and r refer to feed, permeate, and retentate, respectively, and subscript j refers to a component in the gas mixture.

If the membrane has a higher permeability for one of the components in the feed mixture than for others, this component is enriched in the permeate and depleted in the retentate. Gases can be separated in microporous and in homogeneous membranes. The selectivity of microporous membranes is generally rather low because of the Knudsen diffusion transport mechanism.

For a practical application of gas separation it is of interest:

- To what extent can a given gas mixture be depleted of a certain component?
- To what extent can a given component be enriched in the permeate?
- How much of the original feed stream can be recovered as permeate or retentate?
- Which hydrostatic pressure difference is needed to achieve the desired separation?
- How much membrane area is required for this operation?

There are three crucial parameters that determine the efficiency of a membrane separation process. These are the membrane selectivity $S_{i,k}$, the ratio of the feed to permeate pressure, and the stage cut. The selectivity is given by the membrane properties and can be expressed by:

$$S_{j,k} = \frac{P_j}{P_k} \tag{15}$$

The pressure ratio and the stage cut are operating-related parameter given by:

$$\Phi = \frac{p^{\mathrm{p}}}{p^{\mathrm{f}}} \tag{16}$$

and

$$\theta = \frac{Q^{\mathrm{p}}}{Q^{\mathrm{f}}} \tag{17}$$

where S and P are the membrane selectivity and the permeability, Φ and p the pressure ratio and the hydrostatic pressure, θ and Q the stage cut and the gas flow rate, and subscripts j, k, p, and f refer to the components j and k, the permeate, and the feed.

The membrane separation factor $\alpha_{\mathrm{j,k}}$ and the membrane enrichment factor $\beta_{\mathrm{j,k}}$ are related to the membrane selectivity and the pressure ratio by:

$$\alpha_{jk} = \frac{X_j^{\mathrm{p}} X_k^{\mathrm{f}}}{X_j^{\mathrm{f}} X_k^{\mathrm{p}}} = S_{j,k} \frac{X_j^{\mathrm{p}} \Phi - X_j^{\mathrm{f}} X_k^{\mathrm{f}}}{X_k^{\mathrm{p}} \Phi - X_k^{\mathrm{f}} X_j^{\mathrm{f}}} \tag{18}$$

and

$$\beta_j = \frac{X_j^{\mathrm{p}}}{X_j^{\mathrm{f}}} = \frac{\alpha_{j,k}}{1 + (\alpha_{j,k} - 1) X_j^{\mathrm{f}}} \tag{19}$$

where α is the separation factor, β the enrichment factor, S the membrane selectivity for a binary mixture, Φ the pressure ratio, X the molar fraction, subscripts k and j refer to two components, and superscripts f and p to the feed and the permeate.

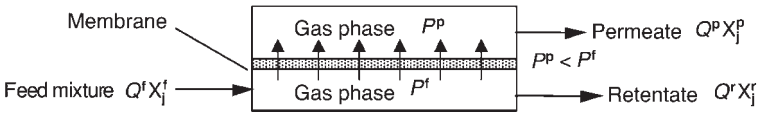

Figure 8. Schematic illustrating gas separation as a unit operation

The pressure ratio Φ has a value between 0 and 1. Thus, the maximum separation and enrichment is achieved when the pressure ratio approaches zero. The effect of the pressure ratio on the enrichment or the separation that can be achieved in a separation process depends also on the construction of the membrane module and the mode of operation, such as cocurrent or countercurrent or complete mixing of feed and permeate. This makes the calculation of the enrichment as a function of the pressure ratio rather complex and requires numerical solutions which are described in detail in the literature or provided by companies selling gas separation equipment [1, 4–6]. Only for very simple cases such as complete mixing of permeate and retentate or for a very low stage cut can the composition of the permeate be calculated to a first approximation by [7]:

$$X_j^{\mathrm{p}} = \frac{X_j^{\mathrm{f}}\Phi}{2} + \frac{1}{2} + \frac{\Phi}{2(S_{j,k}-1)} - \left[\left(\frac{X_j^{\mathrm{f}}\Phi}{2} + \frac{1}{2} + \frac{\Phi}{2(S_{j,k}-1)}\right)^2 - \frac{S_{j,k}\Phi X_j^{\mathrm{f}}}{(S_{j,k}-1)}\right]^{0.5} \qquad (20)$$

A practical application of gas separation is the enrichment of oxygen in air using a silicone rubber membrane which has a selectivity of 2. The molar fraction of oxygen in air is assumed to be 0.2 and the stage-cut is assumed to be 0. In Figure 9 the calculated enrichment factor β and the separation factor α are shown as a function of the pressure ratio.

The example of oxygen enrichment in air illustrated in Figure 9 shows that the maximum separation and maximum enrichment can only be achieved when the ratio of permeate over feed approaches 0, that is, when either the feed pressure is infinitely high or the permeate pressure approaches 0 and when the stage cut is 0. The above example also shows that the maximum molar fraction in air that can be achieved in gas separation using a silicone rubber membrane is about 0.33 if the pressure ratio and the stage cut approach 0.

The flux through a membrane is proportional to the pressure difference between the feed and the permeate side, as indicated in → Membrane Separation Processes, 1. Principles, Equation 85. This means that to obtain high fluxes the pressure difference between feed and permeate should be as high as possible, and to obtain high separation the pressure ratio between the permeate and the feed should be as low as possible.

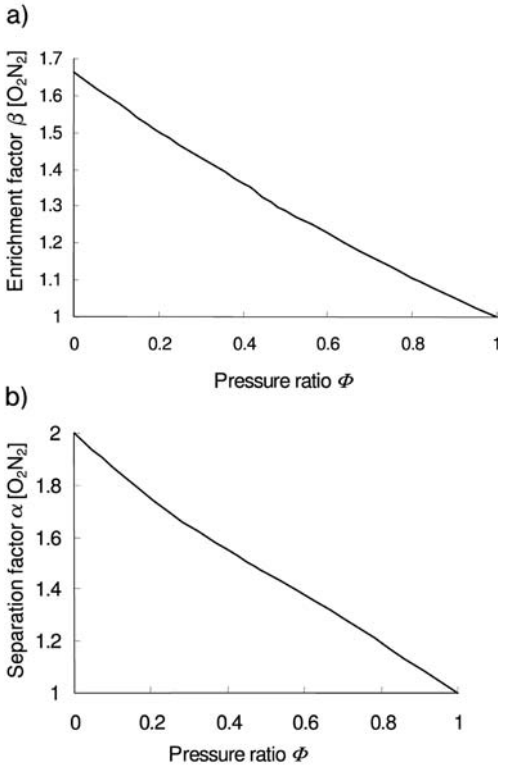

Figure 9. a) The oxygen enrichment factor α and b) the separation factor β as a function of the pressure ratio for a membrane selectivity $S_{O2/N2}$ of 2 and a feed composition of X_{O2}/X_{N2} of 0.2/0.8

In gas separation the achievable separation or enrichment of a component in the permeate or retentate depends not only on the membrane properties and the applied hydrostatic pressure ratio but also on the so-called stage cut, which corresponds to the recovery rate used in filtration processes and which is given by:

$$\theta = \frac{V^{\mathrm{p}}}{V^{\mathrm{f}}} \text{ or } \theta = \frac{Q^{\mathrm{p}}}{Q^{\mathrm{f}}} \qquad (21)$$

if a continuous process as shown in Figure 5 is considered.

Here θ is the stage cut, V and Q are the volume and the volume flux, respectively, and superscripts p and f refer to permeate and feed. The stage cut has a value between 0 and 1.

The molar fraction of a component in the feed, the permeate, and the retentate is related to the

stage cut by the mass balance expressed in Equation (14). Introducing the stage cut in this equation leads to:

$$X_j^f = \theta X_j^p + (1-\theta) X_j^r \quad (22)$$

where X_j is the mole fraction of component j and superscripts f, p, and r refer to feed, permeate, and retentate.

The permeate and retentate concentration as a function of the stage cut is illustrated in Figure 10 for the separation of oxygen and nitrogen. The calculation is based on a membrane selectivity $S_{O2/N2}$ of 2 and a feed composition X_{O2}/X_{N2} of 0.2/0.8. Furthermore, it is assumed that the pressure ratio of permeate and retentate pressure approaches 0 and the retentate and permeate are completely mixed. Under the above conditions the highest oxygen concentration that can be reached in the permeate is 0.33 when the stage cut approaches 0. The lowest oxygen concentration in the retentate of 0.11 is reached when the stage cut approaches 1.

In practical applications gas separation systems are not operated with complete mixing of the permeate and retentate, and the calculation of

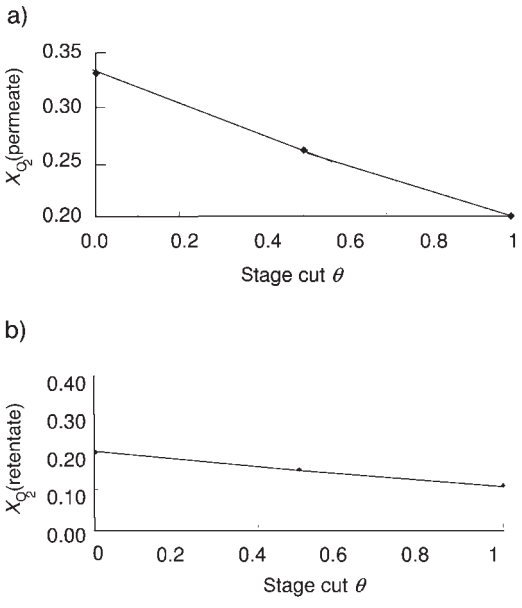

Figure 10. a) The oxygen permeate and b) the oxygen retentate concentration as a function of the stage cut assuming complete mixing of permeate and retentate, for a membrane selectivity $S_{O2/N2}$ of 2, and a feed composition of X_{O2}/X_{N2} of 0.2/0.8

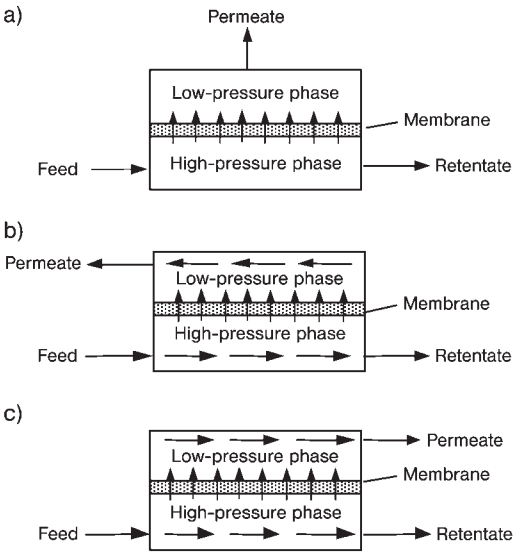

Figure 11. Schematic illustrating three idealized feed and permeate flow patterns used in gas separation systems. a) Complete mixing of feed and permeate; b) Countercurrent plug flow of feed and permeate; c) Cocurrent plug flow of feed and permeate

the permeate and retentate concentrations becomes significantly more complicated and depends on the membrane module design and flow conditions of permeate and retentate. In gas separating modules three idealized flow patterns can be assumed (Fig. 11). The effect of the various flow patterns on the performance of a unit is rather significant. The determination of the required membrane area and separation characteristics for the different flow patterns for binary and multicomponent mixtures are described in the literature, and computer programs for parametric studies are available for all flow patterns [4–6].

The separation obtained in a single permeation stage can be multiplied many times, if necessary, by connecting an appropriate number of stages in series to form a countercurrent *permeation cascade*. There are two possible arrangements. In the first arrangement there is no reflux of the retentate. A typical section of a permeation cascade without reflux of the retentate is shown in Figure 12a. In this simple arrangement the permeate from stage n becomes the feed for the next higher stage $n+1$, and the retentate is disposed of. In the second case the retentate is

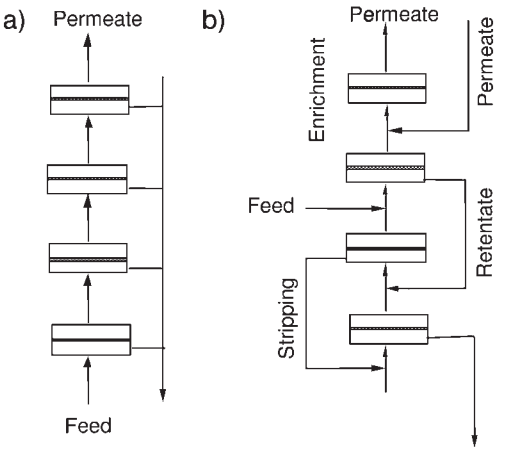

Figure 12. Flow diagram of permeation cascades a) without reflux of the retentate and b) with reflux of the retentate

refluxed, that is, the retentate of stage n is mixed with the next lower stage $n-1$ and so on. All permeate streams must be recompressed before entering a higher stage. The simple cascade without reflux of the retentate is only of use when the retentate is virtually of no value and large enrichment factors or product concentrations in the permeate are required. If a cascade with reflux of the retentate is used there are two sections depending on the position where the original feed solution is introduced into the cascade. One is the so-called enrichment section where the product is enriched in the permeate, and the other is the stripping section where the product is enriched in the retentate. The principle of a permeation cascade with reflux of the retentate is illustrated in Figure 12b.

The number of stages needed for a required separation factor can be determined by the McCabe – Thiele method, a graphical procedure commonly used in the design of distillation columns. The subject of cascade operation is of rather fundamental importance for all separation processes and therefore treated in detail in the corresponding literature [8].

The graphical procedure of determining the number of stages is based on two basic relations. One is the equilibrium curve expressing the relation between the composition of the permeate and the retentate in one stage; this is a function of the membrane properties, operating pressures, stage cut, and flow pattern. The second curve is the operating line, which describes the relation between the composition of the permeate leaving stage n and that of the retentate of the next higher stage. The operating line depends on the operating scheme used in a cascade (e.g., variable or constant stage cut) and is the material balance between two stages. The application of the countercurrent flow principle in a reflux cascade has led to the development of the membrane column [9]. In analogy to distillation a membrane column can be regarded as a reflux cascade with an infinite number of stages, and like a reflux cascade the membrane column will produce an enriched retentate in the stripping section and an enriched permeate in the enrichment section. Compared to the normal cascade the membrane column has the advantage of being able to produce highly enriched products both in the permeate and retentate without pressurizing the permeate before it enters the next stage of the cascade, and it thus requires less energy for compression of the gas. On the other hand, the membrane column requires a significantly higher membrane surface area. Whether a column or a cascade is optimal for a given separation problem must be decided by an economic analysis. It is highly dependent on membrane properties and module design. Although the membrane-column concept can in principle be applied to other membrane separation processes such as reverse osmosis, it is most important for gas separation.

3. Pervaporation

In pervaporation, volatile organic components are removed from a liquid feed mixture through a semipermeable membrane into a gas phase. The separation of components from a liquid mixture is determined not only by differences in their vapor pressures, as is the case in distillation, but also by their permeation rates through the membrane. As in gas separation the driving force for the transport is the chemical potential gradient of the permeating components in the membrane, which can be related to the partial vapor pressures in the liquid and vapor phase. In gas separation, the chemical potential difference is induced by a hydrostatic pressure difference. In pervaporation, however, the chemical potential gradient is usually induced by applying a vacuum on the permeate side of a membrane, or by

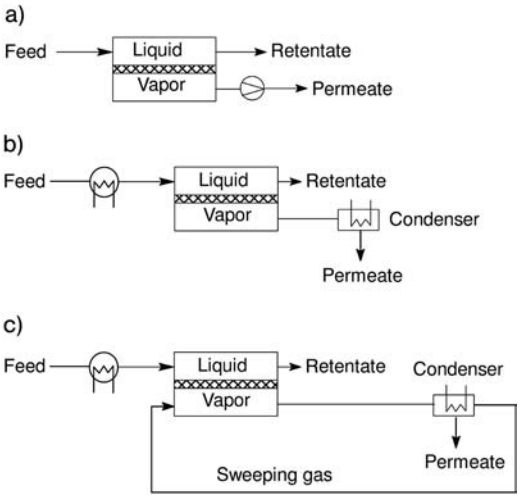

Figure 13. Schematic illustrating different operation modes used in pervaporation: a) vacuum-driven pervaporation, b) temperature-difference-driven pervaporation, and c) sweeping-gas-driven pervaporation

applying a temperature difference between the liquid feed mixture and the permeate gas phase. A sweeping gas can also be used to remove the permeating component. The mass transport in a pervaporation membrane can be described by the same mathematical relations as the gas transport with the exception that the chemical potential in the membrane on the feed side of the membrane is expressed by the molar fraction and the activity coefficient in the liquid phase as discussed in Section 21.

The different modes of operation in pervaporation are illustrated in Figure 13.

4. Dialysis

Dialysis was one of the first technically used membrane separation processes and today is still among the most important commercially. A large fraction of today's artificial kidneys are dialyzers, and hemodialysis is the largest single application of a membrane separation process.

In a dialyzer, one or more solutes are transferred from the feed solution to the dialysate or stripping solution through a membrane under the driving force of a concentration gradient. The principle of the process has been discussed earlier. The mass transfer in a dialyzer is

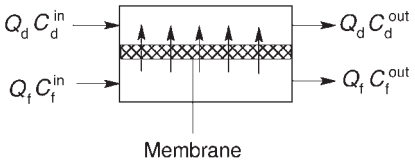

Figure 14. Operating scheme of a dialyzer (Q and C refer to volume flow rate and concentration of the component to be removed, subscripts f and d to feed solution and dialysate, and superscripts in and out to inlet and outlet)

illustrated in Figure 14. A dialyzer cell contains two chambers separated by a membrane. A feed solution to be depleted of a solute is pumped through one chamber while the receiving fluid (dialysate) is passed through the other chamber. The three most common modes of operating a dialyzer are parallel flow and countercurrent flow of feed solution and dialysate and feed flow with the dialysate completely mixed.

The overall efficiency of a dialyzer is governed by two interdependent factors: the ratio of the flow rates of the two fluids and the rate constant for solute transport between the fluids, which is determined by membrane properties, membrane area, fluid channel geometry, and local fluid velocities. A material balance can be expressed by:

$$N_i = Q_f(C_i^f - {}^{out}C_i^f) = Q_d(C_i^d - {}^{in}C_i^d) \tag{23}$$

where N is the overall transport rate of the solute, Q and C are the volume flow rate and the concentration, subscripts i, f, and d refer to a component, the feed solution, and the dialysate, and superscripts f and d, and in and out refer to feed and dialysate, and inlet and outlet. The overall rate of solute transport is also expressed by:

$$N_i = J_i A = k * A\Delta\bar{C}_i \tag{24}$$

where J_i is flux rate and $\Delta\bar{C}_i$ the average concentration difference of component i between the fluids, A the membrane area, and k^* the overall rate constant. The efficiency of a dialyzer is expressed in terms of its *dialysance* D_f, which is defined as [10]:

$$D_f = \frac{N}{C_i^{f} - {}^{in}C_i^{d}} = \frac{k^* A\Delta\bar{C}_i}{C_i^{f} - {}^{in}C_i^{d}} \tag{25}$$

The dimensionless ratio D_f/Q_f is a convenient efficiency parameter, because it represents the fraction of maximum attainable solute depletion actually achieved in the feed.

The proper average solute concentration difference is the logarithmic mean of the inlet and outlet differences. The mean concentration difference between the feed and dialysate solution depends on the membrane module design and the mode of operation, that is, complete mixing of feed and dialysate or co- or countercurrent flow. The calculation of the dialysance for the different operation modes by simultaneous solution of Equations (23) to (25) using the logarithmic mean concentration difference as driving force is described in the literature [10].

In dialysis with cation- or anion-exchange membranes, which is used to recover acids or bases from a mixture with salts, the recovery rate of the acid or base and the maximum concentration that can be achieved is of interest. The recovery rate is given by:

$$\Delta = \frac{^{out}C_i^d Q^d}{^{in}C_i^f Q^f} \tag{26}$$

where Δ is the recovery rate of the desired product (acid or base), C the concentration, Q the volume flow through the dialysis cell, and superscripts f and d, and in and out refer to feed and dialysate, and inlet and outlet.

The recovery rate Δ determines how much of the acid or base which is in a mixture with a salt can be recovered. Δ has a value between 0 and 1. It is related to the concentration of the recovered product and the concentration in the depleted solution at the cell exit by:

$$^{out}C_i^d = \frac{Q_f}{Q_d}\ \Delta^{in}C_i^f \tag{27}$$

and

$$^{out}C_i^f = (1-\Delta)^{in}C_i^f \tag{28}$$

According to Equations (23) to (28) the concentration of a component such as an acid or base in the final dialysate or the depleted feed solution can be determined as a function of the overall mass transfer coefficient, the total membrane area, and the volume flow rates of the feed and the product for different dialysis operations modes [11].

The modeling of diffusion dialysis only on the basis of concentration differences, as suggested in the literature [11], does not consider electrochemical interactions of the different ions (i.e. a diffusion potential or osmotic and electroosmotic effects) and can therefore only be considered as a first approximation for the design of a diffusion dialysis process.

5. Electrodialysis

The basic concept of electrodialysis is discussed in → Membrane Separation Processes, 1. Principles, Section 3.7. Although there are many different components necessary for the proper operation of an electrodialysis plant such as the electrical power supply, pumps, and control and monitoring devices, the stack is a key component in an electrodialysis unit. For designing and operating an electrodialysis stack certain process parameters must be taken into account and be controlled such as the feed solution concentration and the desired product and brine concentrations. Various modes of operation are possible such as batch or continuous. In many cases the desired desalination or concentration of a feed solution cannot be obtained in a single pass through the electrodialysis cells. To achieve a higher degree of desalination or concentration two or more stacks are placed in series. When high product recovery rates are required part of the brine may be recycled. A cell arrangement of an electrodialysis stack is shown schematically in Figure 15.

An electrodialysis stack is composed of a multitude of cells placed in parallel between two electrodes. The different cells are separated by ion-exchange membranes. In alternating cells a feed solution is concentrated and desalinated, respectively. A spacer-gasket arrangement separates the membranes and contains the manifolds to distribute the process fluids in the different compartments. In designing and operating an electrodialysis stack, several criteria concerning the hydrodynamic and electrical properties must be considered. A proper electrodialysis stack design should provide a maximum effective membrane area per unit stack volume and ensure equal and uniform flow distribution in each compartment. Any leakage between the diluate, concentrate, and the electrode cells should be

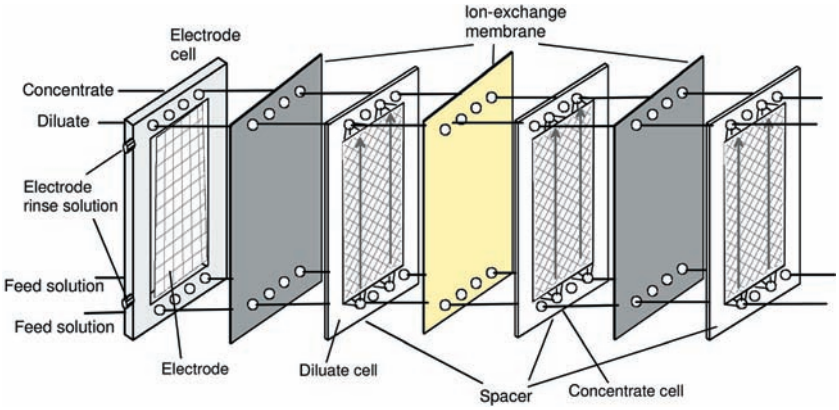

Figure 15. Schematic illustrating the construction of a sheet-flow electrodialysis stack

prevented. The spacer screen should provide maximum mixing of the solutions at the membrane surfaces and should cause a minimum in pressure loss [12, 13]. In practice, two different stack types are used on a large scale: sheet-flow and the tortuous path flow stacks. In a sheet-flow electrodialysis stack the solution flows in a straight path from the entrance to the exit ports, which are located on opposite sides of the gasket, as indicated in Figure 16a.

In the tortuous path flow stack, the membrane spacer gaskets have a long serpentine cutout which defines a long narrow channel for the fluid path and provides higher residence times of the solution in the cells even at high flow velocities. A tortuous path flow spacer gasket is shown schematically in Figure 16b.

The distance between the membrane sheets (cell thickness) should be as small as possible to minimize energy consumption due to electrical resistance of the solutions. In industrial-size electrodialysis stacks, membrane distances are typically between 0.3 and 2 mm. A spacer is introduced between the individual membrane sheets to support the membrane and to control the solution flow distribution.

Solution flow velocities in sheet-flow stacks are typically 3 – 10 cm s^{-1}, whereas in tortuous path flow stacks the solution flow velocities are 15 to 50 cm s^{-1}. Because of higher flow velocities and longer flow paths, higher pressure drops on the order of 2 – 3 bar are obtained in stacks with tortuous path flow spacers compared to sheet-flow systems, which have pressure drops between 0.5 and 2 bar. In a practical electrodialysis system, 200 to 1000 cation- and anion-exchange membranes are installed in parallel to form an electrodialysis stack providing 100 to 500 cell pairs. At each end of a stack is an end-plate that contains the electrodes. Depending on the feed solution composition and the product requirements electrodialysis units can be operated in batch-type, continuous, or feed-and-bleed mode with partial recycle of the diluate and concentrate streams.

In practical applications two basic concepts of electrodialysis are used. One is referred to as unidirectional electrodialysis [14] and the other as electrodialysis reversal [15]. In a unidirectionally operated electrodialysis stack the electrical potential gradient across the stack is permanently applied in one direction, and the diluate and concentrate cells are also permanently fixed over the period of operation. Unidirectionally operated electrodialysis plants are rather sensitive to membrane fouling and

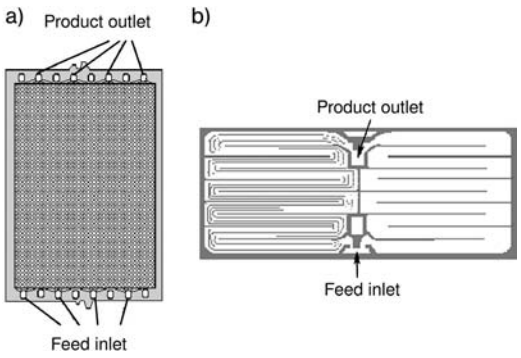

Figure 16. Concept of a) a sheet-flow and b) a tortuous path flow electrodialysis spacer gasket

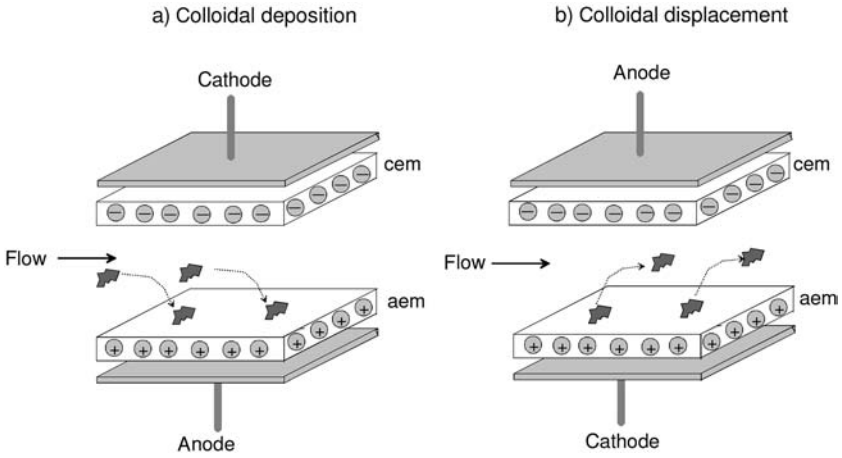

Figure 17. Schematic illustrating the removal of deposited negatively charged colloidal components from the surface of an anion-exchange membrane by reversing the electric field

scaling and often require frequent stack-cleaning procedures. In electrodialysis reversal the change of the electric potential across the stack is accompanied with a reversal of the flow streams, so that the diluate becomes the concentrate and vice versa. In practical applications the polarity is changed at time intervals ranging from a few minutes to several hours. The advantage of electrodialysis reversal is that precipitates in the brine cells are redissolved when the polarity is reversed and the brine cell becomes the diluate cell. During the reversal of the polarity and the flow streams there is a brief period when the concentration of the desalted product exceeds the product quality specification and must be discharged. Thus, in electrodialysis reversal a certain amount of the product is always lost to the waste stream. This is generally no problem in desalination of brackish water, but it may be not acceptable in certain applications in the food and drug industry when feed solutions with high-value products are processed.

The main advantage of electrodialysis reversal is that suspended matter, polyelectrolytes, and multivalent salts that are precipitated on the membrane surfaces are removed when the polarity and the flow streams are reversed. This is illustrated in Figure 17, which shows a typical electrodialysis cell formed by a cation- and anion-exchange membrane between two electrodes. If an electric field is applied to a feed solution containing negatively charged particles or large organic anions these components will migrate to the anion-exchange membrane and be deposited on its surface. If the polarity is reversed the negatively charged components will migrate away from the anion-exchange membrane back into the feed stream and the membrane properties are restored. This procedure is very effective and is used today in almost all electrodialysis water desalination systems.

The degree of desalination that can be achieved in passing the feed solution through a stack is a function of the solution concentration, the applied current density, and the residence time of the solution in the stack, which is determined by the process path length. If the required product concentrations are not achieved in a single process path, electrodialysis can be operated as a multistage process or as a process with feed and bleed in which the diluate or the concentrate or both are partially recycled. Staging can be done by complete physical separation of the stacks, with each having its own set of electrodes, pumps, and power supply, or by internal staging where one set of electrodes and pumps is needed. A disadvantage of simple staging is a constant recovery rate of the feed solution. If variable recovery rates are desired the system must be operated in a feed-and-bleed mode. In this operating mode both the brine and the product concentration can be controlled independently.

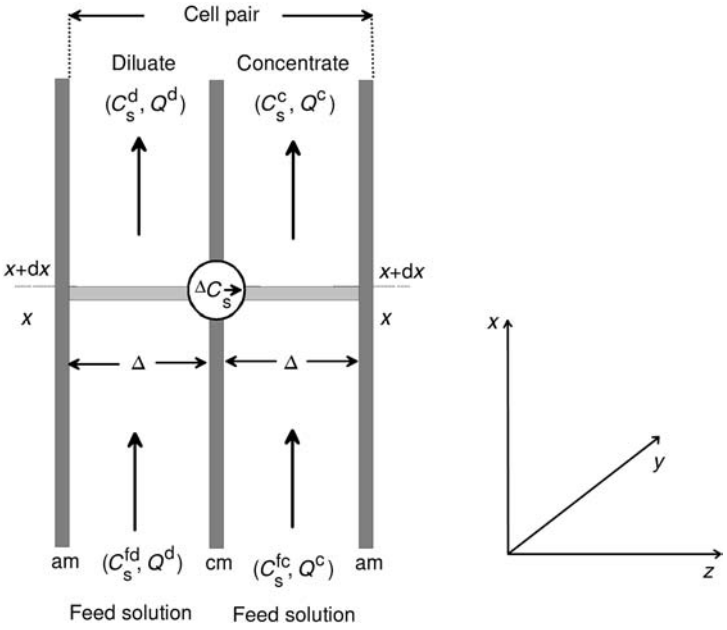

Figure 18. Schematic illustrating the flow of diluate and concentrate streams parallel to the membrane surface in a cell pair of an electrodialysis stack and the concentration change between diluate and concentrate solution $^{\Delta}C_s$ due to the ion flux through the membrane

5.1. Mass Transport in an Electrodialysis Stack

The degree of desalination in electrodialysis can be expressed by a material balance between the feed, the concentrate, and the diluate solutions. It is a function of the residence time of the different solutions in the cells, that is, the flow velocities of the solutions, the membrane area in a cell pair, and the applied current density. Calculation of the complete mass balance between the diluate and concentrate flow stream can be rather complex for multicomponent solutions and high ion concentrations, which means high osmotic pressures and activity coefficients that deviate largely from 1 and when the two flow streams have different flow velocities and directions. However, in many electrodialysis applications the concentrate and diluate cells have identical geometries and flow conditions, that is, the flow in both cells is cocurrent and of identical velocity. The transfer of ions in such a cell arrangement is illustrated in Figure 18.

The figure shows a cell pair of an electrodialysis stack with diluate and concentrate flow streams parallel to the membrane surface in the x direction. The geometry of both cells are identical and the two flow streams have the same flow velocity. It is assumed that the concentration potential between the two flow streams due to different concentrations in the diluate and concentrate solutions is negligibly low compared with voltage drops due to the resistance of the solutions, and that changes in the resistance of the solutions due to the boundary layer effects are also negligible. Finally, it is assumed that all diffusion processes between the two flow streams can be neglected and the only driving force for the transport is the electrical potential gradient, which is constant over the entire cell length.

Under the above-stated assumptions the degree of desalination of a given feed solution, that is, the changes in the ion concentration in the diluate and concentrate cells in an area element expressed in equivalents, can be calculated as a function of the solution properties, the applied voltage, and the stack design by:

$$\mathrm{d}\, C_s^{\mathrm{d}} = -\mathrm{d}\, C_s^{\mathrm{c}} = \mathrm{d}^{\Delta}C_{\mathrm{s}} = J_{\mathrm{s}} \tag{29}$$

Furthermore:

$$J_s = \frac{i\xi}{FQ_{cell}}\, dA_{cell}, dA_{cell} = Y\, dx, \text{ and } i = \frac{U_{cell}}{\frac{\Delta(C_s^c + C_s^d)}{\Lambda_s C_s^c C_s^d} + r^{am} + r^{cm}} \quad (30)$$

where i is the current density, F the Faraday constant, ξ the current utilization, U_{cell} the applied voltage across the cell pair, dA_{cell} a cell pair area element, Δ the thickness of the cell, Λ_s the equivalent conductivity of the solution (average value for the concentration range considered), r^{am} and r^{cm} are the resistances of the anion- and cation-exchange membranes, and dC_s^d and dC_s^c the concentration changes in a volume element of the diluate and concentrate cell, $d^{\Delta}C_s$ is the concentration change in a volume element of the diluate and concentrate cell due to the ion flux through the membrane, Q_{cell} the flow stream in the diluate or concentrate cell, Y the cell width, and dx a distance change in direction of the flow stream parallel to the membrane surface.

Introducing Equation (29) into Equation (30) and integrating over the cell length leads to:

$$\ln\frac{C_s^c C_s^{fd}}{C_s^d C_s^{fc}} + \frac{\Lambda_s(r^{am}+r^{cm})(C_s^{fd}-C_s^d)}{\Delta} = \frac{\Lambda_s \xi U_{cell} YX}{FQ_{cell}\Delta} \quad (31)$$

where $C_s^{fd}$and C_s^{fc} are the concentrations of the diluate and the concentrate at the cell inlet, and C_s^d and C_s^c the concentrations of the diluate and the concentrate at the cell outlet.

The total flow of the diluate or concentrate solution through a stack is given by:

$$Q_{st} = N\, Q_{cell} = N\Delta Y u \quad (32)$$

where Q_{st} is the total solution flow of the diluate or the concentrate through the entire stack, Q_{cell} the flow through one cell, N the number of cells in the stack, Δ the thickness and Y the width of a cell, and u is the linear flow velocity in the cell.

The total voltage across the stack U_{st} is given by:

$$U_{st} = NU_{cell} \quad (33)$$

Equations (31) to (33) give the relations between the various stack construction data such as cell length, cell width, and cell thickness, the solution properties such as the concentrations and conductivities of the feed, the concentrate, and the product, the flow velocity in the cells, and the applied voltage. However, to design an electrodialysis stack for a certain plant capacity on the basis of Equation (33) it must be taken into consideration that the current density cannot exceed a certain value, which is referred to as limiting current density. Since the applied voltage is related to the current density it should not exceed a certain value.

The current density and thus the voltage that can be applied in a practical electrodialysis, however, is limited due to concentration polarization and ion depletion at the membrane surfaces in the diluate cell. The causes and consequences of the limiting current density are discussed in more detail below.

Introducing the limiting current density into Equation (30) and multiplying by the number of cell pairs in the stack gives the limiting applied voltage across the stack $U_{st,lim}$:

$$U_{st,lim} = i_{lim}\frac{N\Delta}{\Lambda_s}\left[\frac{C_s^d}{C_s^c} + 1 + \frac{\Lambda_s C_s^d}{\Delta}(r^{am}+r^{cm})\right] \quad (34)$$

where i_{lim} is the limiting current density, C_s^d and C_s^c are the concentrations in the diluate and concentrate solutions, Λ_s is the equivalent conductivity of the salt solution, r^{am} and r^{cm} are the area resistances of the anion- and cation-exchange membranes, Δ is the cell thickness, and $\mathfrak{R}$ the number of cell pairs in the stack.

Combination of Equations (31), (33), and (34) and rearranging gives the required membrane area of the complete stack as function of the cell geometry, the applied voltage, the concentrations of the feed, concentrate, and diluate solutions, and the solution flow velocities:

$$A_{st} = N_{cell}\frac{\left[\ln\frac{C_s^c C_s^{fd}}{C_s^d C_s^{fc}} + \frac{\Lambda_s(r^{am}+r^{cm})(C_s^{fd}-C_s^d)}{\Delta}\right]}{\left[\frac{C_s^d}{C_s^c} + 1 + \frac{\Lambda_s C_s^d}{\Delta}(r^{am}+r^{cm})\right]}\,\frac{Yu\Delta u\Delta_s^d}{\xi\, i_{lim}} \quad (35)$$

where A_{st} is the total cell pair area installed in the stack, N_{cell} the number of cell pairs in the stack, C_s^{fd} and C_s^{fc} are the concentrations of the diluate and the concentrate at the cell inlet, C_s^d and C_s^c are the concentrations of the diluate and the concentrate at the cell outlet, Λ_s is the equivalent conductivity of the salt solution, r^{am} and r^{cm} are the area resistances of the anion- and cation-exchange membranes, Δ is the cell thickness, i.e., the distance between the cation- and anion-exchange membrane, Y the cell width, u the

linear flow velocity, F the Faraday constant, i_{lim} the limiting current density, and ζ the current utilization.

From the cell pair area required for a certain plant capacity and the cell dimensions the process path length L_{pp} can be determined by:

$$L_{pp} = \frac{A_{cell}}{Y} \tag{36}$$

It becomes equal to the cell length X when desalination is achieved in one pass through the cell.

5.2. Energy Requirements in an Electrodialysis Desalination Process

The total energy requirements in a practical electrodialysis process is the sum of four terms:

- The energy required for the transport of ions from a feed to a concentrate solution.
- The energy necessary to pump the solutions through the stack from a feed solution reservoir to the product tank and brine disposal.
- The energy consumed by the electrode reactions.
- The energy required to operate various process control and measuring instruments.

The last two terms can generally be neglected in larger capacity plants. However, they can be significant in specific applications of small-capacity plants used in the chemical industry or in the treatment of certain wastewater streams.

The required electrical power for the transfer of ions in a desalination process is given by the total current passing through the stack multiplied by the applied voltage. The total current passing through a cell pair is given by:

$$I = \frac{N_{cell} Q_{cell} F (C_s^{fd} - C_s^{d})}{\xi} \tag{37}$$

where I is the total electric current passing through the cell pair, Q_{cell} the flow rate of the solution in the diluate cell, C_s^{fd} and C_s^{d} are the diluate feed and product equivalent concentrations, and N_{cell} is the number of cell pairs in the stack.

The electric power P_{des} required for the desalination process in a stack is given by:

$$P_{des} = N_{cell} U_{cell} I = \frac{F Q_{cell} (C_s^{fd} - C_s^{d})}{\xi} N_{cell} U_{cell} \tag{38}$$

Introducing Equations (30) and (31) into (38) and rearranging gives the power requirement for the desalination process in a cell pair:

$$P_{des} = N_{cell} U_{cell} I = \frac{N_{cell}}{A_{cell}} \left[\frac{\Delta \ln \frac{C_s^{fd} C_s^{c}}{C_s^{fc} C_s^{d}}}{\Lambda_s (C_s^{fd} - C_s^{d})} + r^{am} + r^{cm} \right] \left[\frac{Q_{cell}^{d} F (C_s^{fd} - C_s^{d})}{\xi} \right]^2 \tag{39}$$

Multiplying the power requirements for one cell pair with the time of operation and the number of cell pairs in the stack gives the energy required for the amount of product obtained in this time:

$$E_{des} = N_{cell} U_{cell} I\, t = \frac{N_{cell} t}{A_{cell}} \left[\frac{\Delta \ln \frac{C_s^{fd} C_s^{c}}{C_s^{fc} C_s^{d}}}{\Lambda_s (C_s^{fd} - C_s^{d})} + r^{am} + r^{cm} \right] \left[\frac{Q_{cell}^{d} F (C_s^{fd} - C_s^{d})}{\xi} \right]^2 \tag{40}$$

Thus, the specific energy required for a unit volume of product is:

$$E_{des/spce} = \frac{N_{cell} U_{cell} I}{Q_{st}} = \frac{N_{cell}}{A_{cell} Q_{st}} \left[\frac{\Delta \ln \frac{C_s^{fd} C_s^{c}}{C_s^{fc} C_s^{d}}}{\Lambda_s (C_s^{fd} - C_s^{d})} + r^{am} + r^{cm} \right] \left[\frac{Q_{cell}^{d} F (C_s^{fd} - C_s^{d})}{\xi} \right]^2 \tag{41}$$

where E_{des} and $E_{des/spec}$ are the desalination costs for electrodialysis and the cost per unit volume of product, I is the total current and U_{cell} the voltage per cell, N_{cell} the number of cell pairs in a stack, t the time of operation, C_s^{fd} and C_s^{fc} are the equivalent concentrations of the diluate and the concentrate at the cell inlet, C_s^{d} and C_s^{c} the concentrations of the diluate and the concentrate at the cell outlet, Λ_s is the equivalent conductivity of the salt solution, r^{am} and r^{cm} are the area resistances of the anion- and cation-exchange membranes, Δ is the cell thickness, ζ the current utilization, Q_{cell} and Q_{st} are the diluate flow velocities in a cell and in the entire stack, respectively, and A_{cell} is the cell pair area.

The energy needed to pump the various flow streams through the stack is given by:

$$E_{p/spce} = \frac{E_p}{Q^d t} = k_{eff} \frac{(Q^d \Delta p^d + Q^c \Delta p^c + Q^e \Delta p^e)}{Q^d} \qquad (42)$$

where $E_{p/spec}$ is the total energy per unit diluate water for pumping the diluate, the concentrate, and the electrode rinse solution through the stack, k_{eff} an efficiency term for the pumps, and Q^d, Q^c, and Q^e are the volume flow rates of the diluate, the concentrate, and the electrode rinse solution through the stack.

The energy consumed by the electrode reaction and required for the operation of the control and measuring instruments is generally neglected or taken as a fixed item which is between 1 and 3 % of the energy used for ion transfer and pumping of the solutions.

5.3. Electrodialysis Process Costs

The total production costs in electrodialysis are the sum of fixed charges associated with amortization of the plant investment costs and of operating costs such as energy and maintenance requirements. The investment costs include nondepreciable items such as land and depreciable items such as the electrodialysis stacks, pumps, electrical equipment, monitoring and control devices, and membranes. The required membrane area for a given plant capacity is inversely proportional to the current density and directly proportional to the quantity and quality of the product from a given feed solution.

The total operating costs of the electrodialysis plant include energy and maintenance costs and all pre- and post-treatment procedures. They are also a function of the membrane properties, feed and product composition, and several process and equipment design parameters such as stack construction. A dominant role in electrodialysis process costs is played by the applied current density, since it directly affects the investment and energy costs. The required membrane area decreases with increasing current density, while the consumed energy increases with increasing current density, as shown by Equations (35) and (41). Thus, the total product costs, which are the sum of energy costs, amortization, and maintenance costs, are a function of the current density and will reach a minimum at a certain current density. This is schematically shown in Figure 19.

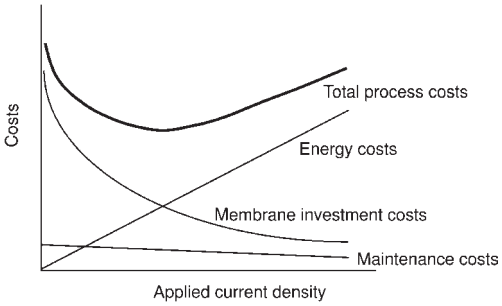

Figure 19. Schematic illustrating the process costs in electrodialysis as a function of the applied current density

Here the total process costs, the energy costs, the amortization on membrane and hardware investment, and the maintenance costs are shown as function of the applied current density. The optimum operating current density in electrodialysis depends to a large extent on the equipment, especially the membrane cost and life, and on the cost of energy. The current density to be applied in electrodialysis is determined by the limiting current density, which should not be exceeded because of possible pH changes in the diluate and concentrate. However, in certain cases it is possible to operate well above the limiting current density [16].

In many applications, electrodialysis competes with other separation processes. Although the theoretically required minimum energy is identical in all processes, the irreversible energy dissipation differs considerably. The desalination of a saline solution by, for example, reverse osmosis involves the passage of water through a membrane under the driving force of a hydrostatic pressure difference, whereas in electrodialysis the salt passes through a membrane under the driving force of an electrical potential difference. The irreversible energy loss in reverse osmosis is caused by hydraulic resistance of the membrane to the water flux and is thus independent of the feed salt concentration. In electrodialysis the irreversible energy loss is proportional to the number of ions transferred from a feed to a concentrate solution, and thus for a given product water concentration it is directly proportional to the feed water concentration. For feed solutions with low salt concentrations the

energy requirements are therefore generally lower for electrodialysis than for reverse osmosis; with feed solutions having a high salt concentration the situation is reversed.

Comparison of energy consumption in mass separation processes must consider the fact that in electrodialysis energy is required in the form of electricity, a relatively expensive form, whereas processes such as distillation use heat, a relatively inexpensive form.

6. Bipolar Membrane Electrodialysis Process Design

The basic concept of electrodialytic water dissociation with bipolar membranes is discussed in → Membrane Separation Processes, 1. Principles, Section 3.8. The main application of this process is the production of an acid and a base from the corresponding salt in a cell arrangement consisting of cation- and/or anion-exchange membranes and bipolar membranes in alternating series between two electrodes forming an array of individual cells. A repeating unit may be composed of a three-cell arrangement (Fig. 20a) or a two-cell arrangement (Fig. 20b and c) [17]. In the three-compartment cell design one cation-exchange, one anion-exchange, and one bipolar membrane with three flow streams in between them (i.e., the salt solution, the acid, and the base) represent a cell unit. In the two-compartment cell design a cation-exchange and a bipolar membrane, or an anion-exchange membrane and a bipolar membrane with two flow streams in between are arranged in parallel. One of the flow streams contains the salt solution in a mixture with the produced acid or base. In a three-cell arrangement relatively pure acids and bases are obtained. However, an additional monopolar membrane is needed which will increase the investment cost. The two-cell arrangement results in an acid or a base in a mixture with the salt. The two-cell arrangement is often applied when the product has a relatively low conductivity. This is, for instance, the case when certain organic acids which have a low degree of dissociation such as lactic acid are recovered from a fermentation broth. Without additional salt the poor conductivity in the acid compartment would result in excessive power consumption.

As in conventional electrodialysis various modes of operation are possible such as batch, feed-and-bleed, and continuous processes [18].

The stack design used in electrodialysis with bipolar membranes is basically the same as that of the sheet-flow stack used in conventional electrodialysis, with the exception that the basic unit of an electrodialysis stack with bipolar membranes consists generally of three cells. Therefore, three separate flow streams must be fed through the manifold in the individual cells that form the repeating unit of the stack. The current density used in electrodialysis with bipolar membranes for the production of acids and bases is generally an order of magnitude higher than in most conventional electrodialysis applications. The voltage drop across a cell unit is also higher than in conventional electrodialysis because of the additional resistance of the bipolar membrane and the concentration potential between the reaction layer of the membrane and the outer phases. As a consequence of the high current density the cell unit area is usually significantly lower in bipolar membrane electrodialysis than that of conventional electrodialysis. Because of the higher voltage drop over a cell unit in electrodialysis with bipolar membranes the number of repeating cell units is also much lower than in conventional electrodialysis.

To design a bipolar membrane electrodialysis plant of a certain capacity and given feed solution and product requirements the necessary membrane area and the applied voltage must be determined. For a stack of three-cell units the required membrane area can be expressed as the cell unit area, which consists of a cation-exchange membrane, an anion-exchange membrane, and a bipolar membrane. The cell unit area is related to the total current required for the production of a certain amount of an acid and a base by the current density.

$$A_{\text{cell}} = \frac{I}{i} \tag{43}$$

where A_{cell} is the cell unit area, I is the total current passing through the stack or stacks in series, and i is the average current density.

The total current for a certain production capacity is given by:

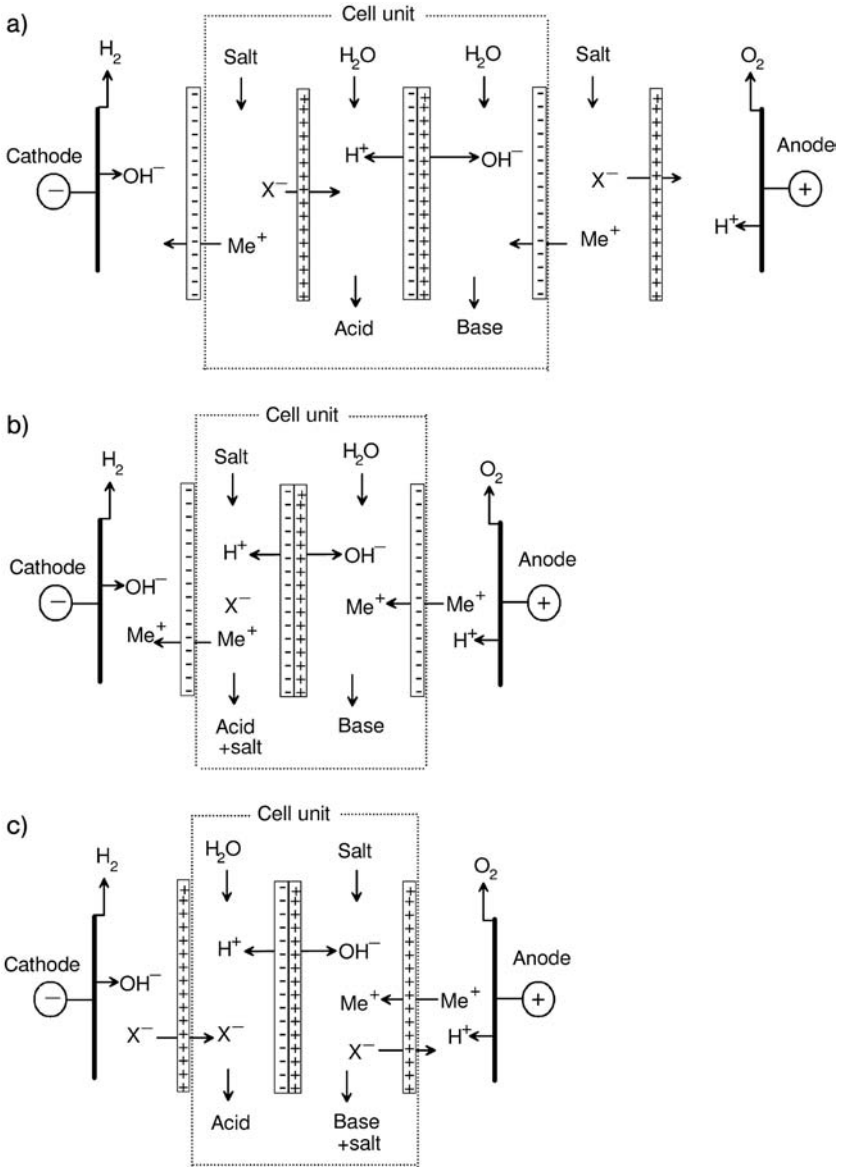

Figure 20. Schematic illustrating the cell arrangement in an electrodialytic water dissociation stack
a) A three-cell unit composed of an anion-exchange, a cation-exchange, and a bipolar membrane; b) A two-cell unit composed of a cation-exchange and a bipolar membrane; c) A two-cell unit composed of an anion-exchange and a bipolar membrane

$$I = \frac{Q_p F \Delta C_p}{N_{cell} \xi} \tag{44}$$

where Q_p is the total product flow, ΔC_p the concentration difference between the product solution in the feed at the entrance of the first stack and at the exit of the final stack, N the number of cell units in a stack, F the Faraday constant, and ξ the current utilization.

The average current density can be determined from the applied voltage and the resistance of the cell unit.

When concentration potentials between the three solutions are neglected the total voltage drop consists of three major contributions:

- The potential drop due to the water dissociation equilibrium

- The potential drop due to the resistance of the solutions
- The potential drop due to the resistance of the membranes

A cell unit contains the salt, the acid and base solutions, and the three membranes between these solutions. The total voltage drop is the sum of the water dissociation potential and the voltage drop due to the resistance of the solutions and membranes.

The voltage drop across a cell unit of a stack which consists of geometrically identical cells operated in cocurrent flow is given by:

$$U_{\text{cell}} = \bar{i}\left[\Delta\left(\frac{1}{\Lambda_s C_s}+\frac{1}{\Lambda_b C_a}\right)+r^{\text{tr}}+r^{\text{am}}+r^{\text{cm}}+r^{\text{bml}}\right] + \frac{RT}{F}\ln\frac{C^{\text{tr}}_{\text{H}^+}C^{\text{tr}}_{\text{OH}^-}}{C^{\text{b}}_{\text{H}^+}C^{\text{b}}_{\text{OH}^-}} \tag{45}$$

where U_{cell} is the voltage drop across a cell unit, $\bar{i}$ the average current density along the cell in direction of the flow velocity parallel to the membrane surface, Δ the thickness of the individual cells, C the average concentration, Λ the equivalent conductivity, r the area resistance, R the gas constant, T the absolute temperature, F the Faraday constant, superscripts tr, am, cm, bml, and b refer to transition region, cation-exchange membrane, anion-exchange membrane, the two layers of the bipolar membrane, and the bulk solution, respectively, and subscripts s, a, and b to salt, acid, and base, respectively.

The average concentration is given by the integral average over the process path length. The average concentration for each ion is:

$$\bar{C}_i = \frac{C_i^{\text{f i}} - C_i^{\text{pi}}}{\ln\left(\frac{C_i^{\text{fi}}}{C_i^{\text{pi}}}\right)} \tag{46}$$

where $\bar{C}_i$ is the average concentration of ion i in a cell, C_i^{fi} and C_i^{pi} are the concentrations in the bulk solution at the cell entrance, i.e., the beginning of the process path length and the cell exit, i.e., the exit of the process path length.

Introducing Equation (46) into Equation (45) leads to:

$$U_{\text{cell}} = \bar{i}\left[\Delta\left(\sum_i \frac{\ln\left(\frac{C_i^{\text{fi}}}{C_i^{\text{pi}}}\right)}{\Lambda_i\left(C_i^{\text{fi}}-C_i^{\text{pi}}\right)}\right)+r^{\text{tr}}+r^{\text{am}}+r^{\text{cm}}+r^{\text{bml}}+\frac{RT}{iF}\ln\frac{C^{\text{tr}}_{\text{H}^+}C^{\text{tr}}_{\text{OH}^-}}{\frac{C^{\text{fH}^+}_{\text{H}^+}-C^{\text{pH}^+}_{\text{H}^+}}{\ln\frac{C^{\text{fH}^+}_{\text{H}^+}}{C^{\text{pH}^+}_{\text{H}^+}}}\frac{C^{\text{fOH}^-}_{\text{OH}^+}-C^{\text{pOH}^-}_{\text{OH}^-}}{\ln\frac{C^{\text{fOH}^-}_{\text{OH}^-}}{C^{\text{pOH}^-}_{\text{OH}^-}}}}\right] \tag{47}$$

where U_{cell} is the voltage drop across a cell unit, $\bar{i}$ is the average current density in the cell unit, and subscript i refers to salt, acid, and base. All other symbols are as defined in Equations (44) and (45).

The required membrane area and the process path length for a given capacity plant and given feed solution and product concentrations as a function of the current density are derived from Equations (43) and (44):

$$A = \frac{Q_{\text{p}}F\left(C_{\text{p}}^{\text{fp}}-C_{\text{p}}^{\text{p}}\right)}{\bar{i}\ \xi} \tag{48}$$

where A is the cell unit area, Q_{p} is the product volume flow, F is the Faraday constant, $C_{\text{p}}{}^{\text{fp}}$ and $C_{\text{p}}{}^{\text{p}}$ are the concentrations of the product at the cell entrance and the product at the cell exit, $\bar{i}$ is the average current density, ξ the current utilization, and N_{cell} the number of cell units in a stack.

For a given stack design and number of cell units in the stack the required process path length is given by:

$$L_{\text{pp}} = \frac{A}{YN_{\text{cell}}} \tag{49}$$

where L_{pp} is the process path length, Y the cell width, Q_{p} the product volume flow, F the Faraday constant, $C_{\text{p}}{}^{\text{fp}}$ and $C_{\text{p}}{}^{\text{p}}$ are the concentrations of the salt at the beginning and the end of the process path length; and N_{st} is the number of stacks in series.

6.1. Operating Modes in Bipolar Membrane Electrodialysis

There are several operating modes for the bipolar membrane stack. Depending on the feed solution concentration and the product requirements the process may be operated in a batch or continuous mode. In practical applications it is often operated in a feed-and-bleed mode as illustrated in Figure 21.

With partial recycling of the acid, the base, and the salt solution a constant product concentration can be achieved by adjusting the feed and bleed streams and accordingly changing the

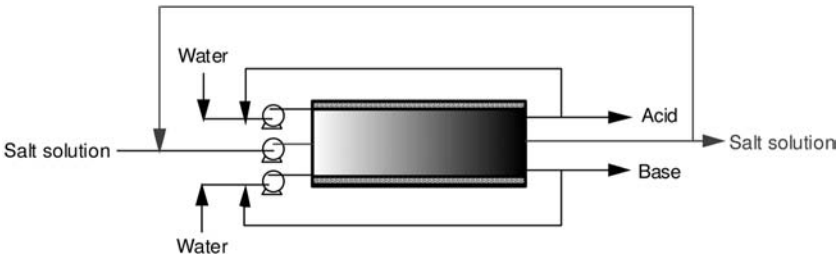

Figure 21. Flow scheme of a bipolar membrane electrodialysis stack operated in a feed-and-bleed mode, i.e., with partial recycling of the acid, the base, and the salt solution

recirculation rates of the acid, the base, and the salt solution flow streams.

6.2. Energy Requirements in Electrodialytic Water Dissociation

The energy required in electrodialytic water dissociation with bipolar membranes is the sum of three terms:

- The electrical energy required to transfer salt ions from the feed solution and protons and hydroxide ions from the bipolar membrane into the acid and base solutions.
- The energy required for the water dissociation in the bipolar membrane.
- The energy consumption for pumping the solutions through the stack.

Energy consumption due to electrode reactions can generally be neglected when more than 50 – 100 cell units are stacked between the two electrodes [11]. The energy required for the dissociation of water at constant temperature and pressure can be calculated for solutions with different H^+ ion activities (i.e., pH values). The Gibbs free energy required for the production of acids and bases in a bipolar membrane is:

$$\Delta G = -RT\ln\frac{C^{tr}_{H^+}C^{tr}_{OH^-}}{C^{b}_{H^+}C^{b}_{OH^-}} = -2.3\,RT\,\Delta\,\mathrm{pH} \qquad (50)$$

where ΔG is the Gibbs free energy, R the gas constant, T the absolute temperature, F the Faraday constant, $C^{tr}_{H^+}$, $C^{tr}_{OH^-}$, $C^{b}_{H^+}$, and $C^{b}_{OH^-}$, are the proton and hydroxide ion concentrations in the transition region of the bipolar membrane and the bulk solutions in contact with the bipolar membrane, and ΔpH is the difference between the pH values of the two solutions separated by the bipolar membrane.

The Gibbs free energy for water dissociation varies slightly, depending on the salt being processed, the concentration of acid and base generated, and the temperature. For the production of 1 N acids and bases at 25 °C the theoretical free energy varies between 0.056 and 0.058 kW·h mol^{-1} and the electromotive force between 2.1 and 2.2 V.

6.3. Total Energy Required for Production of an Acid and a Base

The total energy required for acid and base production includes energy losses due to the resistances of the solutions and membranes and is given by the current passing through the stack multiplied by the total voltage drop encountered between the electrodes:

$$E_{pro} = I\,U\,t \qquad (51)$$

where E_{pro} is the energy consumed in a stack for the production of an acid and a base, I the current passing through a stack or a series of stacks, U the voltage applied across the stack (i.e., between the electrodes), and t the operating time.

The voltage drop in a stack arrangement is caused by the electrical resistances of the solutions and the membranes in the stack and by the potentials which are established between solutions of different ion concentrations. The voltage drop per cell unit under the assumption that the stacks consist of geometrically identical cells which are operated in cocurrent flow with equal velocity is given by Equation (46). The required current for the production of a given amount of acid and base is given by Equation (44).

Introducing Equations (44) and (46) into Equation (51) and considering the voltage drop across the entire stack, the total energy for the production of a given amount of acid and base from the corresponding salt solution is given by:

$$E_{pro} = I\,N_{cell}\,U_{cell}\,t = N_{st}\bar{i}\left(\frac{\Delta}{\sum_i \Lambda \bar{C}_i} + r^{tr} + r^{am} + r^{cm} + r^{bml} + \frac{2.3\,RT\bar{\Delta}pH}{\bar{i}\,F}\right)\left(\frac{Q_p F(C_p^{fp} - C_p^{p})}{N_{cell}\,\xi}\right)t \quad (52)$$

where E_{pro} is the energy for the production of a certain amount of acid and base, I the current passing through the stack, N_{cell} the number of cell units in a stack, U_{cell} the voltage drop across a cell unit, $\bar{i}$ the average current density, Δ the thickness of the individual cells, $\bar{C}_i$ the average concentration, Λ_i the equivalent conductivity, r the area resistance, ξ the current utilization, R the gas constant, T the absolute temperature, F the Faraday constant, $\bar{\Delta}$ pH the average difference in the pH value between the solution in the transition region of the bipolar membrane and the two adjacent bulk solutions, subscript i refers to salt, acid, and base, superscripts tr, am, cm, and bml to the transition region, the cation-exchange membrane, the anion-exchange membrane, and the two layers of the bipolar membrane, C_p^{fp} and C_p^{p} are the concentrations of the acid or base at the cell inlet and the cell outlet, Q_p is the total flow of the acid or base through the stack, and t the time.

The total current I passing through the stack, which is identical to the current through a cell unit, is related to the average current density $\bar{i}$ and the area of a cell A_{cell} unit by:

$$I = \frac{Q_p F(C_p^{fp} - C_p^{p})}{N_{st}\,\xi} = \bar{i}\,A_{cell} \quad (53)$$

Introducing Equation (53) into (52) gives the energy for the production of a certain amount of acid and base:

$$E_{pro} = N_{st}\,A_{cell}\left(\frac{\Delta}{\sum_i \Lambda \bar{C}_i} + r^{tr} + r^{am} + r^{cm} + r^{bml} + \frac{2.3\,RT\,\bar{\Delta}pH}{\bar{i}\,F}\right)\left(\frac{Q_p F(C_p^{fp} - C_p^{p})}{A_{cell}\,N_{st}\,\xi}\right)^2 t \quad (54)$$

where the symbols are as defined in Equation (52).

The term $\frac{Q_p F(C_p^{fp} - C_p^{p})}{A_{cell}\,N_{st}\,\xi}$ is identical to the current density. This means that for a given stack design the acid and base production energy E_{pro} is proportional to $\bar{i}^2$.

The average concentrations of the acid, the base, and the salt in the bulk solutions $\bar{C}_i$ can be expressed by an integral average of the solutions at the cell inlet and the cell outlet C_i^{fi} and C_i^{pi}, respectively, as indicated by Equation (47). Thus, the electrical energy consumption for the production of an acid and a base in electrodialytic water dissociation with bipolar membranes can by calculated as a function of the applied current density, the produced acid and base concentrations, and the volume of acid and base, and by the current utilization, which is affected by hydraulic leaks between the cells, current flow through the manifold system, and transport of co-ions, especially protons and hydroxide ions, through membranes that are not strictly permselective. All these effects are expressed in the current utilization ξ.

6.4. Total Process Costs

The estimation of the total production costs in bipolar membrane electrodialysis follows the general procedure applied in conventional electrodialysis. The main difference is that in addition to the monopolar membranes bipolar membranes are needed and that the energy costs are increased by the additional energy required for water dissociation in the bipolar membrane.

Furthermore, the applied current density is only limited by water diffusion into the bipolar membrane and is generally significantly higher than in conventional electrodialysis. The optimum operating current density in bipolar membrane electrodialysis in practical applications is on the order of 1000 A m^{-2} [19].

7. Continuous Electrodeionization Process Design

Continuous electrodeionization is widely used today to produce high-quality deionized water for the preparation of ultrapure water in the electronics industry and in analytical laboratories [20–22].

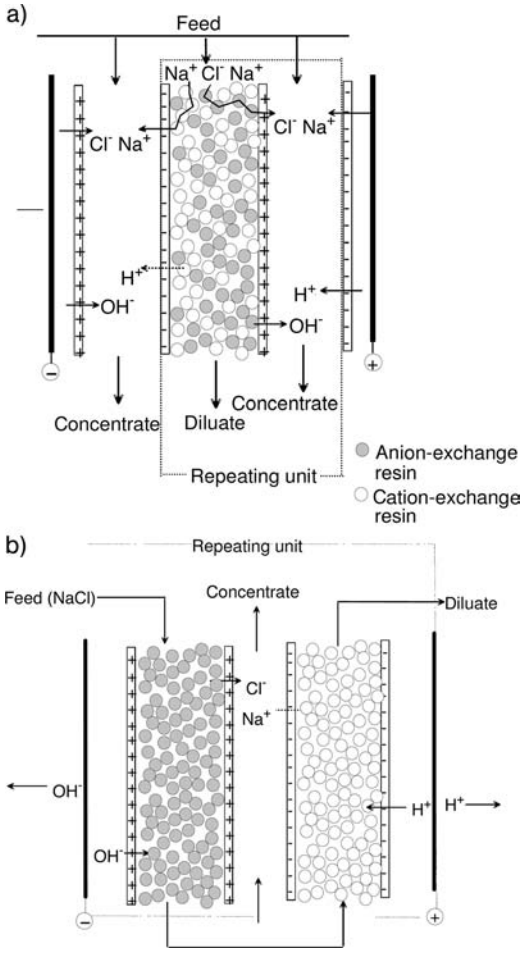

Figure 22. Schematic illustrating two different stack concepts used in continuous electrodeionization. a) A stack in which a repeating unit consists of a diluate cell filled with a mixed bed of ion-exchange resins and a concentrate cell; b) A repeating unit of a stack with a concentrate cell between two diluate cells, one filled with a cation-exchange resin and the other with an anion-exchange resin, between two electrodes

The process design and the different hardware components needed in electrodeionization are very similar to those used in conventional electrodialysis. The main difference is the stack construction. The diluate cell, and sometimes also the concentrate cell, is filled with an ion-exchange resin, which affects the flow distribution and the pressure drop of the solution in the cell drastically. Therefore, the dimensions of the diluate and concentrate cells are generally quite different. The different concepts used for the distribution of the cations and anions in the cell are illustrated in Figure 22. In the conventional electrodeionization process the diluate cell is filled with a bed of mixed ion-exchange resins with a ratio of cation- to anion-exchange resin close to 1, as shown in Figure 22a. The cation- and anion-exchange resins can also be placed in separate beds in series in a stack as is illustrated in Figure 22b. The main difference between the electrodeionization system with the mixed ion-exchange resin bed and the system with separate beds is that in mixed-bed electrodeionization systems anions and cations are simultaneously removed from the feed while the solution leaving the diluate cell is neutral. In the electrodeionization system with separate anion- and cation-exchange beds the anions are first exchanged by the hydroxide ions generated at the cathode, and the solution leaving the cation-exchange bed is basic. This solution is then passed through the cell with the cation-exchange resin, where the cations are exchanged by the protons generated at the anode. At the exit of the cation-exchange cell the solution is again neutral. The production of the H^+ and OH^- ions can also be accomplished by bipolar membranes instead of electrodes [23].

References

General References

1 R. W. Baker: *Membrane Technology and Applications*, J. Wiley & Sons, Chichester, U.K., 2004.

2 H. Strathmann: *Trennung von molekularen Mischungen mit Hilfe von Membranen*, Steinkopff Verlag, Darmstadt, Germany 1979.

3 M. C. Porter, A. S. Michaels: "Membrane Ultrafiltration", *Chem. Technol.* **1** (1971) 56, 248, 440, 633.

4 C. T. Blaisdell, K. Kammermeyer: "Counter-Current and Co-Current Gas Separation", *Chem. Eng. Sci.* **28** (1973) 1249.

5 S. T. Hwang, K. Ksammermeyer: "Membranes in Separations", *Techniques of Chemistry*, Vol. VII, Wiley-Interscience, New York 1975.

6 S. Weller, W. A. Steiner: "Separation of Gases by Fractional Permeation Through Membranes", *J. Appl. Phys.* **21** (1950) 279.

7 H. Strathmann, W. Gudernatsch, C.-M. Bell, K. Kimmerle: "Die Entwicklung von lösungsmittelselektiven Membranen und ihre Anwendung in der Gastrennung und Pervaporation", *Chem. Ing. Tech.* **60** (1988) 590.

8 J. H. Perry: *Chemical Engineers Handbook*, McGraw-Hill, New York 1950.

9 S. T. Hwang, J. M. Thormann: "The Continuous Membrane Column", *AIChE J.* **26** (1980) 558.

10 A. S. Michaels, *Trans. Am. Soc. Artif. Intern. Organs* **12** (1966) 387.

11 H. Strathmann: "Ion-Exchange Membrane Separation Processes", *Membrane Science and Technology Series* **9**, Elsevier, Amsterdam 2004.
12 E. L. Huffmann, R. E., Lacey: "Engineering and Economic Considerations in Electromembrane Processing", in R. E. Lacey, S. Loeb (eds.): *Industrial Processing with Membranes*, John Wiley & Sons, New York 1972, pp. 39–55.
13 L. H. Schaffer, M. S. Mintz: "Electrodialysis", in K. S. Spiegler (ed.): *Principles of Desalination*, Academic Press, New York 1966, pp. 3–20.
14 J. R. Wilson: "Design and Operation of Electrodialysis Plants", in J. R. Wilson, (ed.): *Demineralization by Electrodialysis*, Butterworth Publishers, London 1960.
15 H. Strathmann: "Electrodialysis and Related Processes", in R. D. Nobel, S. A. Stern (eds.): *Membrane Separation Technology: Principles and Applications*, Elsevier, Amsterdam 1995.
16 T. Aritomi, T. van den Boomgaard, H. Strathmann: "Current-Voltage Curve of Bipolar Membrane at High Current Density", *Desalination* **104** (1996) 13.
17 B. Bauer, H. Holdik, A. Velin: "Cell Equipment and Plant Design in Bipolar Membrane Technology", in A. J. B. Kemperman (ed.): *Handbook Bipolar Membrane Technology*, Twente University Press, Enschede 2000
18 K. N. Mani: "Electrodialysis Watersplitting Technology", *J. Membrane Sci.* **58** (1991) 117
19 J. J. Krol, M. Jansink, M. Wessling, H. Strathmann: "Behavior of Bipolar Membranes at High Current Density, Water Diffusion Limitation", *Sep. Purif. Technol.* **14** (1998) 41.
20 US 4 632 745, 1986 (A. J. Giuffrida., A. D. Jha, G. C. Ganzi).
21 US 4 747 929, 1988 (K. K. Siu, A. D. Dracut, G. C. Ganzi).
22 US 3 291 713, 1966 (E. J. Parsi).
23 S. Thate: "Untersuchung der electrochemischen Deionisation zur Reinstwasserherstellung", Ph.D.-Thesis, University of Stuttgart, Germany 2002.
24 T. Sata: "Ion-Exchange Membranes and Separation Processes with Chemical Reactions", *J. Appl. Electrochem.* **21** (1991) 283. 91

Further Reading

E. Drioli, L. Giorno: *Membrane operations*, Wiley-VCH Verl., Weinheim 2009.
B. D. Freeman, ë. P. ëÎìAmpol'skiæi: *Membrane gas separation*, Wiley, Hoboken, NJ 2010.
S. P. Nunes, K.-V. Peinemann: *Membrane technology in the chemical industry*, 2., rev. and extended ed., Wiley-VCH, Weinheim 2006.
A. K. Pabby S. H. Rizvi (Editor), A M Sastre (Editor) *Handbook of Membrane Separations: Chemical, Pharmaceutical, Food, and Biotechnological Applications* CRC Press, Boca Raton 2007.
Y. P. Yampolskii: *Materials science of membranes for gas and vapor separation*, Wiley, Chichester 2006
A. B. Koltuniewicz, E. Drioli: *Membranes in clean technologies*, Wiley-VCH, Weinheim 2008.