MEMBRANE-BASED DESALINATION PROCESSES

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Keywords : Concentration polarization, Electrodialysis, Reverse Osmosis, Membrane, Salt Rejection

Contents

Summary

Desalination processes which use semipermeable membranes have been discussed. These mainly include reverse osmosis for seawater and electrodialysis for brackish water. The effect of various factors and different approaches for modeling are outlined.

1. Introduction

In general, compared to distillation-based separation methods, membrane processes have the following advantages:

- Separation is achieved on the basis of molecular size, shape and charge. It can be carried out at ambient or modest temperatures and therefore damage to heat

sensitive solutes is avoided.

- Since no change of phase is required, energy requirements are modest. This of course, takes into consideration that the processes are power driven and the power production consumes two or three times its value as fossil fuel. It is estimated that if 10 per cent of all distillation/evaporation operations was replaced by membrane processes it would save 2×10^{17} J per year of energy, equivalent to 34×10^{6} barrels of oil per year.
- Membrane processes do not produce any additional waste products.
- Equipment used is modular, hence capacity is scaled up by using multiple units. Processes can be carried out in continuous or batch mode and are easily arranged in either set-up.
- Equipment is compact and system size is directly related to membrane surface area; therefore, the space requirement is small. Moreover, the inventories needed are low.

Membrane processes also have their own limitations, which are discussed in Some Practical Aspects of Desalination Processes.

Where desalination is concerned, the two major applicable processes are reverse osmosis (RO) and electrodialysis (ED), the principles of which are illustrated in Figures 1 and 2 of Separation Phenomena in Desalination. Regarding the range of application, ED is used most effectively and economically when relatively small amount of salt are to be removed from feed water of neither a very high nor a low salinity, such as brackish waters of a few thousand ppm total dissolved solids (TDS) to produce potable water of a few hundred ppm. For seawater desalination containing 30 000 to 45 000 ppm TDS, RO is the most suitable process.
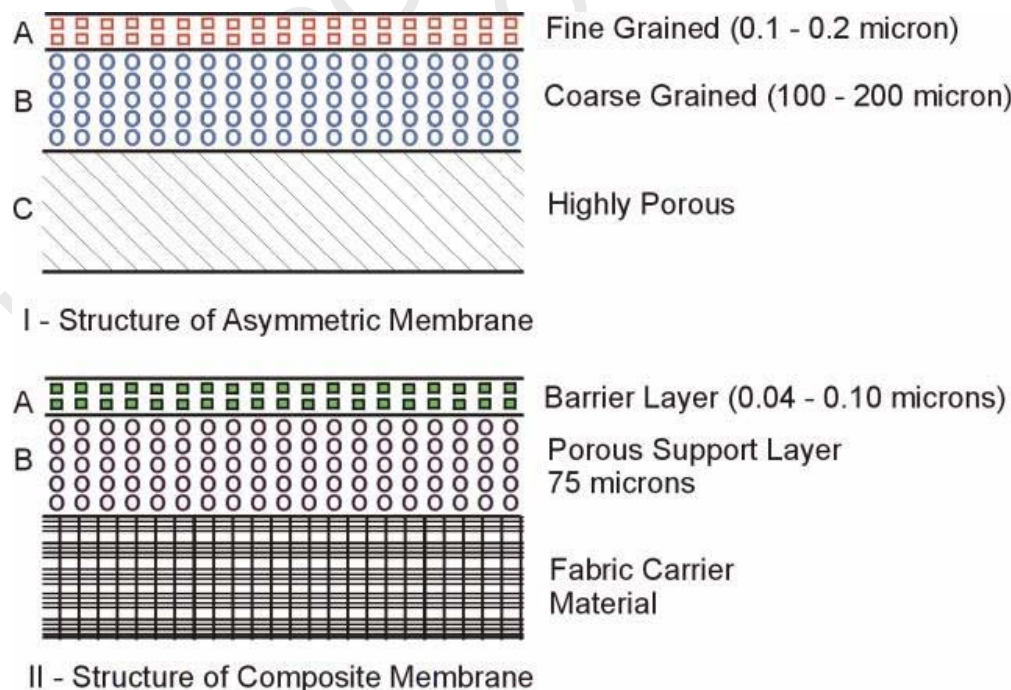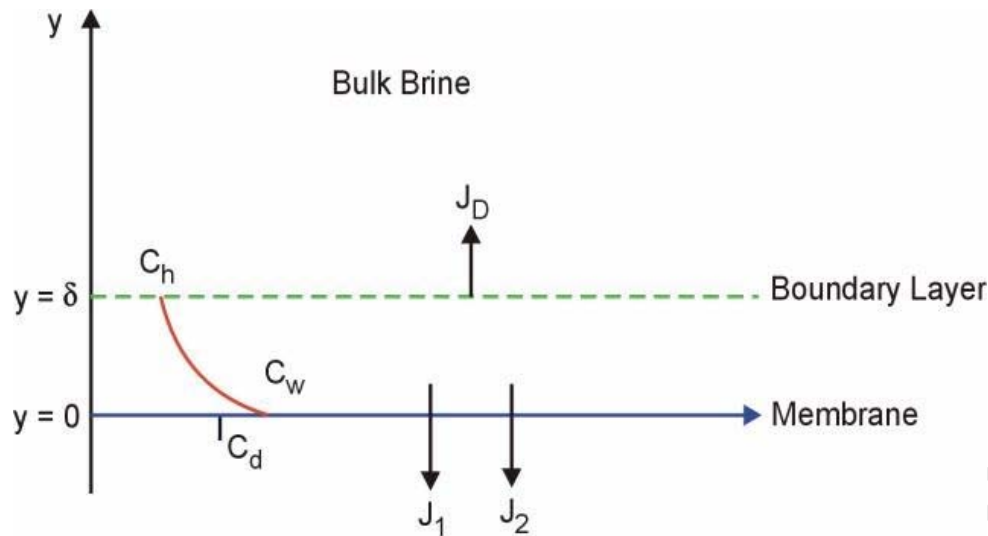

Figure 1. RO membranes.

Figure 2. Effect of CP at steady-state.

1.1. Membrane

The membrane is a thin sheet-like material having typically a thickness of the order of 0.1 mm. It forms a physical barrier between the fluids on either side, at the same time keeping a degree of communication between them. The crucial feature of a particular membrane is its selective permeability to certain species. The "ion-exchange" membranes are most permeable to ions, either cations or anions. On the other hand, selective permeability of other membranes is on the basis of species size. For instance, ultrafiltration membranes allow the passage of water molecules and other small molecular substances including ions (hydrated) but block larger molecules and colloidal particles. The osmotic membranes have good permeability for water molecules, but not for ionic substances and most other molecules.

Driving force	Flux	Relationship	Proportionality constant
Concentration difference (dC)	Mass (J_D)	Fick's law $$J_D = -D\frac{dC}{dX}$$	Diffusion coefficient (D)
Electric potential (dE)	Charge transfer (I)	Ohm's law $$I = R\frac{dE}{dX}$$	Resistance (R)
Temperature difference (dT)	Heat (Q)	Fourier's law $$Q = -k\frac{dT}{dX}$$	Thermal conductivity (K)
Pressure difference (dP)	Volume (V)	Hagen-Poiseuille's law $$V = KdP$$	Hydrodynamic permeability (k)

Table 1. Phenomenological relationships.

In addition to the selective permeability of a membrane, a certain force is needed for the movement of species through the membrane. The flux of any species, i.e. flow rate per unit area of the membrane, is proportional to the driving force. The available driving forces are due to differences in the concentration, electrical potential, pressure or temperature. Table 1 gives the phenomenological relationships of these driving forces.

The overall driving force in the transport of certain species across the membrane is the chemical potential (or free energy) gradient, which is the sum of existing gradients such as concentration, pressure and electrical potential. A concentration gradient, for instance, does not necessarily cause mass flow through a membrane since it may be counterbalanced by a pressure difference (osmotic equilibrium) or by an electrical potential difference (membrane potential). Therefore, in RO, water molecules are forced through the membrane by applying pressure. Similarly, in ED, anions and cations move selectively through an anion-permeable membrane (APM) and a cation-permeable membrane (CPM), respectively, under the influence of an electrical potential. The transport characteristics of different species (last column in Table 1) also play a role in facilitating their separation through a membrane.

The attributes of a perfect membrane for either RO or ED are:

- Chemically, physically, and thermally stable;
- Strong enough to withstand sufficient pressure difference;
- Not affected by fouling;
- Inexpensive.

In addition, the RO membranes should be totally impermeable to salt and infinitely permeable to water. Conversely, the ED membranes should be totally impermeable to water and selectively permeable to cations or anions, and have low electrical resistance. However, no membrane is perfect. All real membranes have a limited life due to mechanical damage and/or suffer from chemical, biological, and thermal deterioration; they are also expensive. The RO membranes would be slightly permeable to salt and require substantial pressure differences in order to obtain reasonable water fluxes. The ED membranes may allow some transport of water and the type of ions that a perfect membrane would exclude.

In short, potentially important properties of membranes are:

- Porosity and pore-size distribution: influence flux, separation, and fouling;
- Hydrophilic-phobic character: influences solute membrane interactions, fouling, and cleaning;
- Surface charge: affects separation and fouling;
- Chemical compatibility: affects operation and cleaning;
- Ease of fabrication and cost: influences economics.

1.2. RO Membranes

The membranes for RO are of two basic types: asymmetric and composite.

Their basic structures are shown in Figure 1. The asymmetric membrane (Figure 1-I) contains three layers; the fine grained layer A is 0.1 to 0.2 micron thick which is made on a porous substrate (layer B) 100 to 200 microns in thickness. The B layer is in between A and a highly porous C layer. In desalination, the concentrated brine is fed to the A layer. The sublayer B only acts as a support and does not affect the separation. Improvement in one layer in the asymmetric membrane is at the expense of the other. These membranes are not reversible in action.

In the composite membrane (Figure 1-II), each layer is made in separate stages. First, a porous support layer is formed; which is then coated with a much thinner active layer.

Cellulose acetate (CA) was the first material used to produce asymmetric membranes to desalinate water by RO. When producing composite membranes the support layer is made of CA and cellulose nitrate which is coated with an active layer of cellulose triacetate. Other composite membranes are produced by making a porous substrate and then chemically treating the surface to form an active layer.

The asymmetric membranes made of CA for RO application have two weaknesses, namely, their susceptibility to hydrolysis and an irreversible compaction of the porous layer at high pressure. The latter results in a decline in water permeability and hence a loss of flux. The successful alternatives to CA are polyamides (aromatic nylons) containing the characteristic chain of CO-NH between aromatic rings. They are now used to make thin film composite membranes for application in seawater desalination units. However, these are sensitive to attack by chlorine and easily clogged by suspended matter.

1.3. ED Membranes

The membranes used for ED are of two types - homogeneous and heterogeneous. The homogeneous membranes consist of a uniform structure of microporous polymer containing about 50 per cent water. The commonly used polymer is polystyrene based, and the homogenous films are cast on a layer of reinforcing fabric. The ion transfer sites are evenly distributed across a cross-linked polymer plastic base for strength.

The heterogeneous membranes are made by mixing particles (less than 20 microns in size) of powdered ion exchange resin, either anion or cation type, with a polymeric binder such as polypropylene. It is cast into a thin sheet which is subsequently treated in order to have controlled porosity for facilitating transport of the selected ions through the membrane. The pores formed are, in fact, microcracks between the resin particles and the polymer matrix. An anion permeable membrane has been developed based on aliphatic rather than aromatic chemistry, which possesses improved properties in several respects.

The ion selectivity is achieved by fixing ions of the opposite charge with a high density. For instance, a CPM is negatively charged; as a result, anions are rejected while the cations are able to enter the membrane and are transported across it. Likewise, APM has a fixed positive charge to prevent the flow of cations through the membrane.

2. Reverse Osmosis (RO) Theory

Three important parameters that characterize the performance of an RO unit are flux, salt rejection and recovery. These are explained below:

2.1. Flux

The water flux is expressed as follows:

$$J_1 = K_1(\Delta P - \Delta\Pi) \tag{1}$$

where

J_1 = water flux, kg m^{-2} (membrane surface) per sec.
ΔP = pressure difference across the membrane, atms
$\Delta\Pi$ = difference in osmotic pressure on two sides of the membrane, atms
K_1 = pure water permeability of the membrane, kg m^{-2} sec atms^{-1}

For some membranes, K_1 is sensitive to pressure with the flux decreasing with an increase in pressure. For such membranes, a compactness term $f(p)$ is included in eq. (1).

$$J_1 = K_1 f(p)(\Delta P - \Delta\Pi) \tag{1A}$$

The salt flux is found to be approximately proportional to the concentration difference of the solutions in actual contact with the membrane on either side, i.e.

$$J_2 = K_2 \Delta C \tag{2}$$

where

C = concentration, kg m^{-3}
K_2 = proportionality constant, m sec^{-1}.

K_2 cannot be so easily measured for two reasons. First, it is not known for certain that the linear relation of eq. (2) holds at zero water flux. Second, at finite fluxes the measurement of K_2 becomes complicated due to the phenomenon of concentration polarization.

2.2. Concentration Polarization (CP)

In any membrane process, some species permeate through the membrane while others in the feed stream are retained. Thus, it causes depletion of the former and accumulation of the latter species in the boundary layer adjacent to the membrane surface. This phenomenon is known as "concentration polarization", which leads to operational problems and puts some restrictions on the membrane process. In fact, for the membrane to be useful the water flux needs to be far greater than the salt flux.

At steady-state the situation that develops at the membrane surface due to CP is depicted in the diagram in Figure 2. The salt concentration in the bulk brine is C_b, whereas the salt concentration at the membrane surface with an adjacent boundary layer of thickness δ, increases to C_w. Due to this concentration difference near the membrane surface, some salt diffuses back into the bulk solution with a flux J_D. As shown, the flux J_D is in the direction opposite to the water flux J_1 and the salt flux J_2 through the membrane. C_d is the salt concentration in the permeate. The CP produces two adverse effects: (i) The increased salt concentration increases osmotic pressure at the membrane surface; consequently, it reduces the potential ΔP-$\Delta\Pi$ for the water flux, and (ii) contributes to a poorer product quality by increasing C_d.

A non-dimensional measure of polarization is expressed as $\alpha = (C_w - C_b)/C_b$ and is called "degree of polarization".

2.3. Salt Rejection

In the absence of significant polarization the rejection factor (RF) is defined as follows:

$$RF = (C_b - C_d)/C_b.$$

However, when CP is significant,

$$RF = (C_w - C_d)/C_w.$$

RF is a measure of the effectiveness of the membrane for removing salts from water. It is not a property of the membrane alone, but also depends on other operating parameters. For example, for a membrane with fixed K_1 and K_2 in an RO system, the rejection would vary with the water flux or operating pressure; therefore,

$$RF = \frac{J_1 - K_2\rho}{J_1}$$

where ρ is solution density, kg m^{-3}.

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