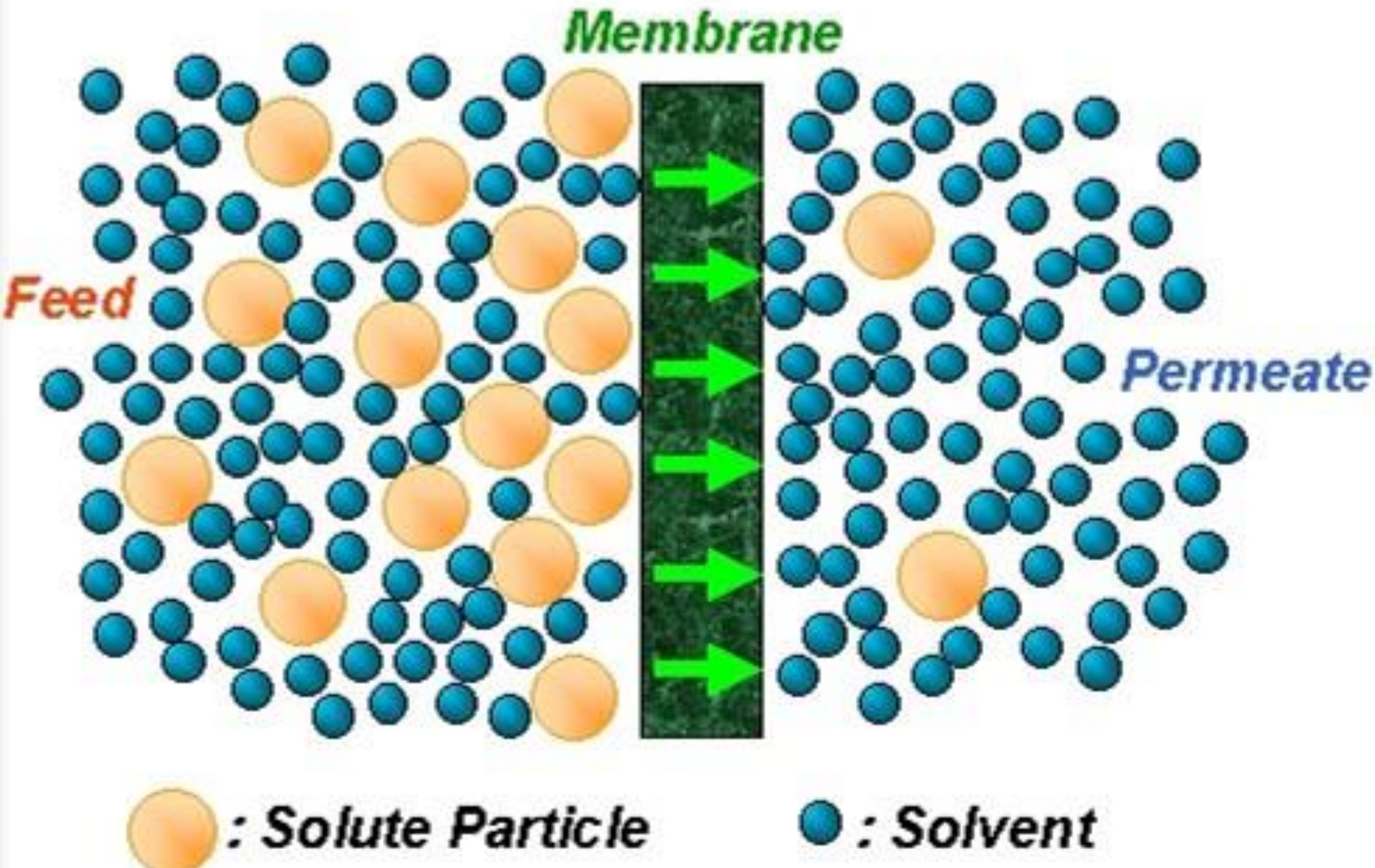
Membrane Processes

- A membrane is a selective barrier that permits the separation of certain species in a fluid by combination of sieving and diffusion mechanisms

- Membranes can separate particles and molecules and over a wide particle size range and molecular weights

Membrane Separation



Membrane Processes

Four common types of membranes:

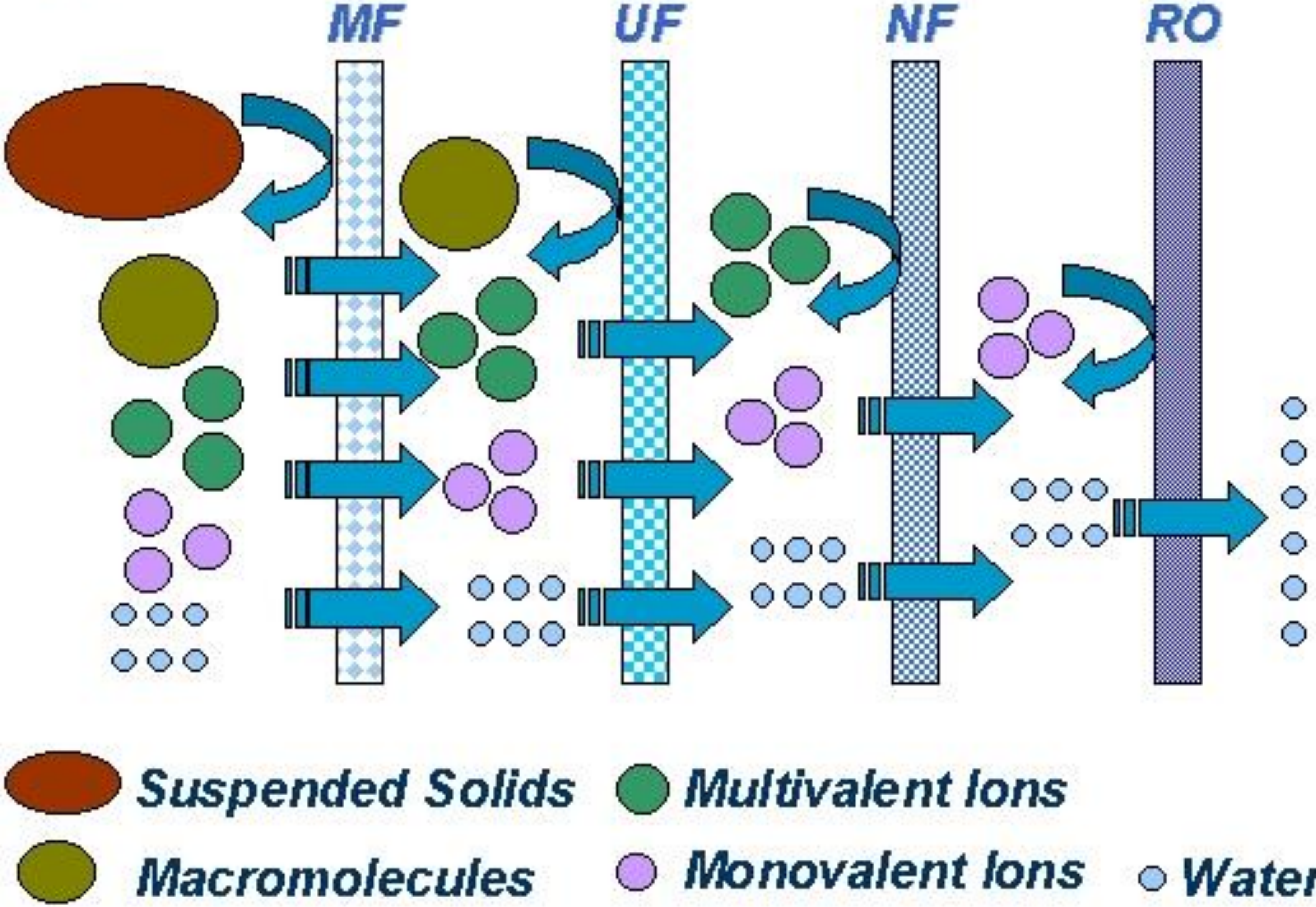
Reverse Osmosis

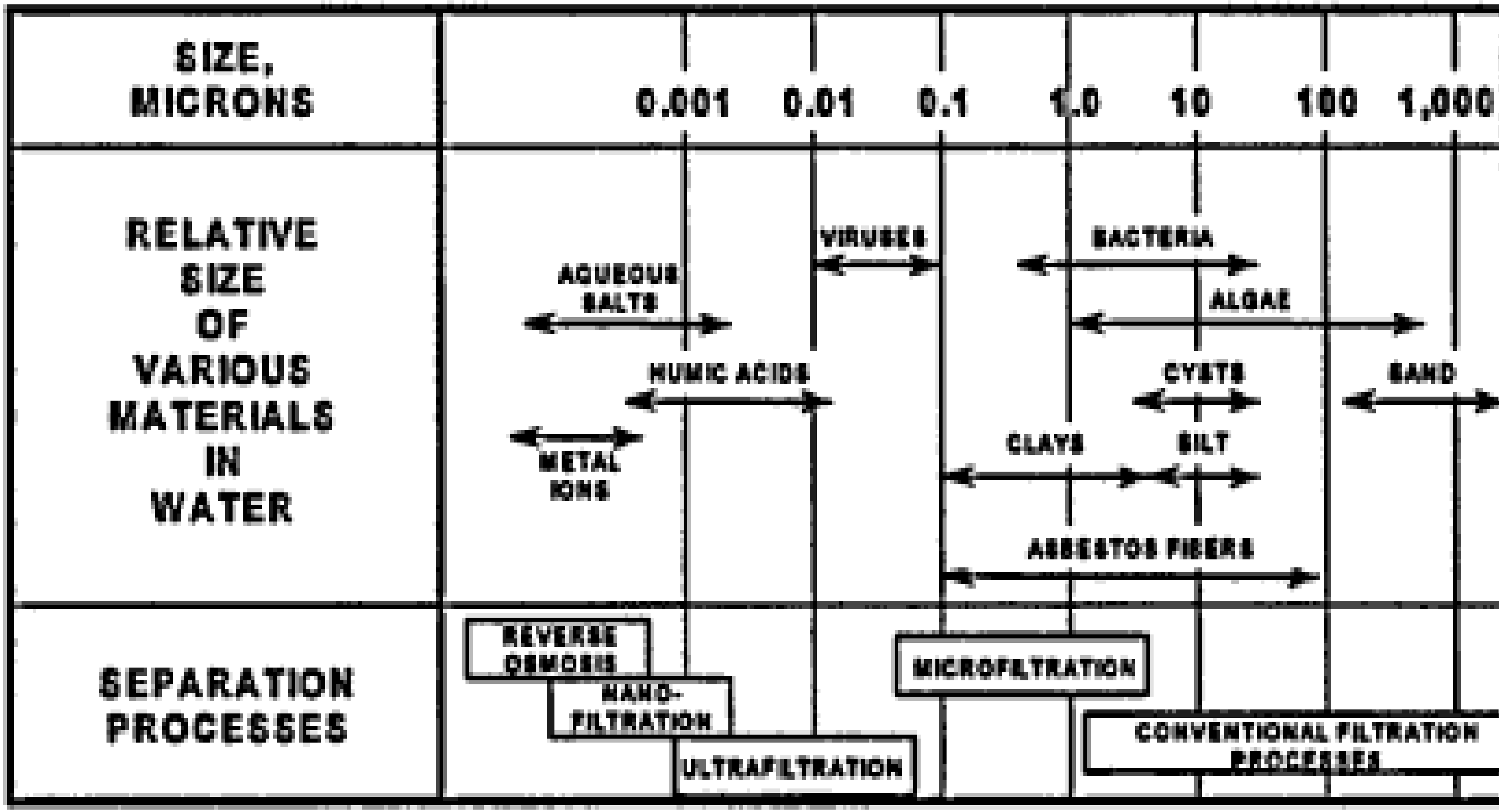
Nanofiltration

Ultrafiltration

Microfiltration

Types of Membrane




SIZE, MICRONS
0.001
0.01
0.1
1.0
10
100
1,000
RELATIVE SIZE OF VARIOUS MATERIALS IN WATER
VIRUSES
BACTERIA
AQUEOUS SALTS
ALGAE
HUMIC ACIDS
CYSTS
SAND
METAL IONS
CLAYS
SILT
ASBESTOS FIBERS
SEPARATION PROCESSES
REVERSE OSMOSIS
NANO-FILTRATION
ULTRAFILTRATION
MICROFILTRATION
CONVENTIONAL FILTRATION PROCESSES

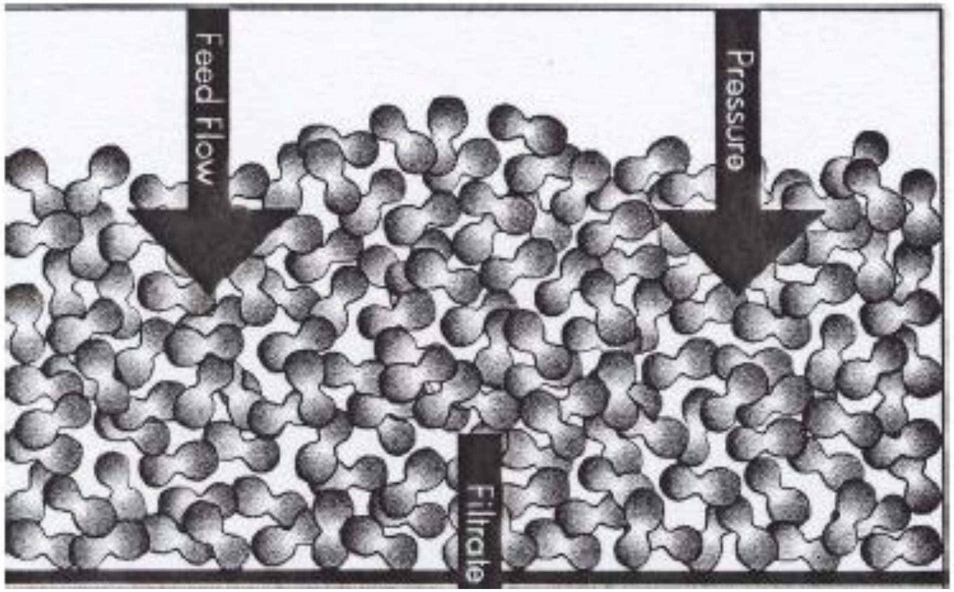
The R.O. membrane is semi-permeable with thin layer of annealed material supported on a more porous sub-structure. The thin skin is about 0.25 micron thick and has pore size in the 5 – 10 Angstrom range. The porous sub-structure is primarily to support the thin skin. The pore size of the skin limits transport to certain size molecules. Dissolved ions such as Na and Cl are about the same size as water molecules.

However, the charged ions seem to be repelled by the active portion of the membrane and water is attracted to it. So adsorbed water will block the passage and exclude ions. Under pressure attached water will be transferred through the pores.

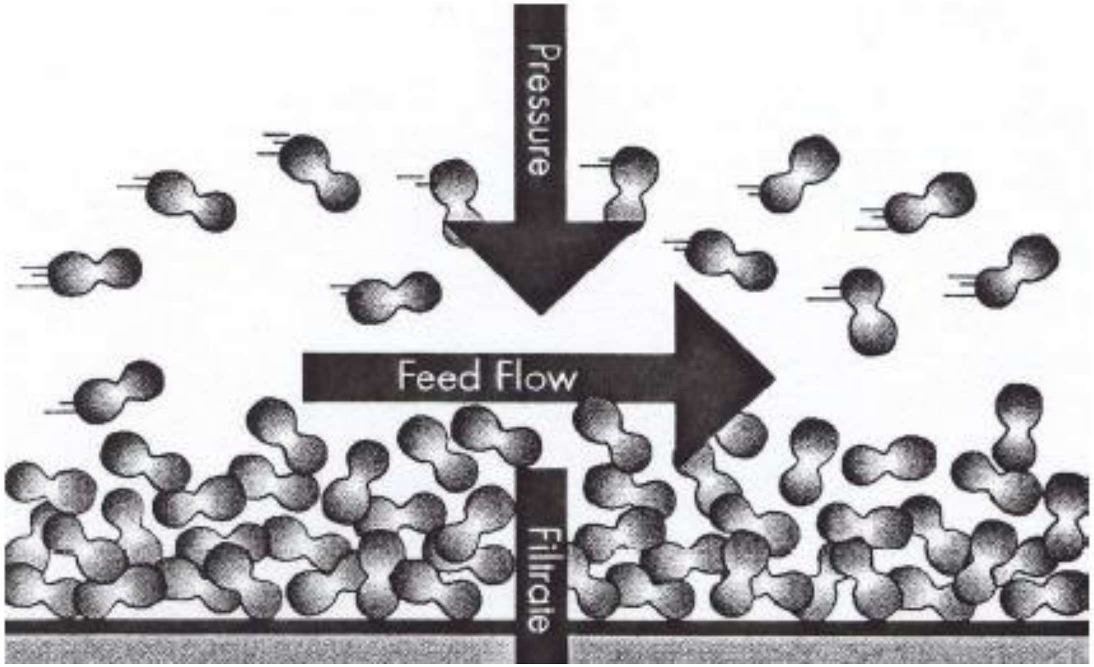
Nanofiltration is a complementary process to reverse osmosis, where divalent cations and anions are preferentially rejected over the monovalent cations and anions. Some organics with MW > 100 -500 are removed There is an osmotic pressure developed but it is less than that of the R.O. process.

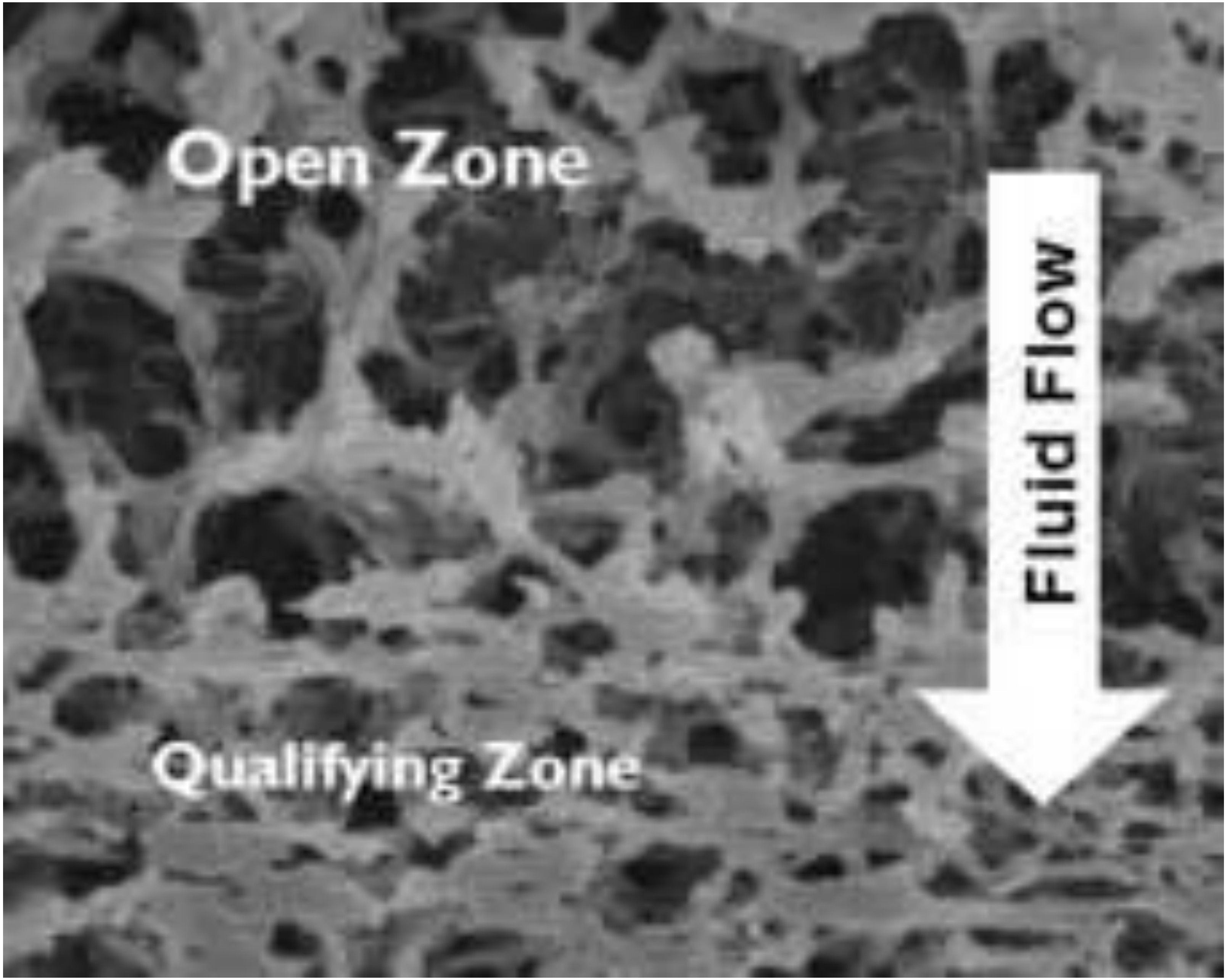
Microfiltration and Ultrafiltration are essentially membrane processes that rely on pure straining through porosity in the membranes. Pressure required is lower than R.O. and due entirely to frictional headloss

Dead-End Membrane Filtration



Cross-Flow Filtration




Open Zone
Fluid Flow
Qualifying Zone

Hollow fiber:

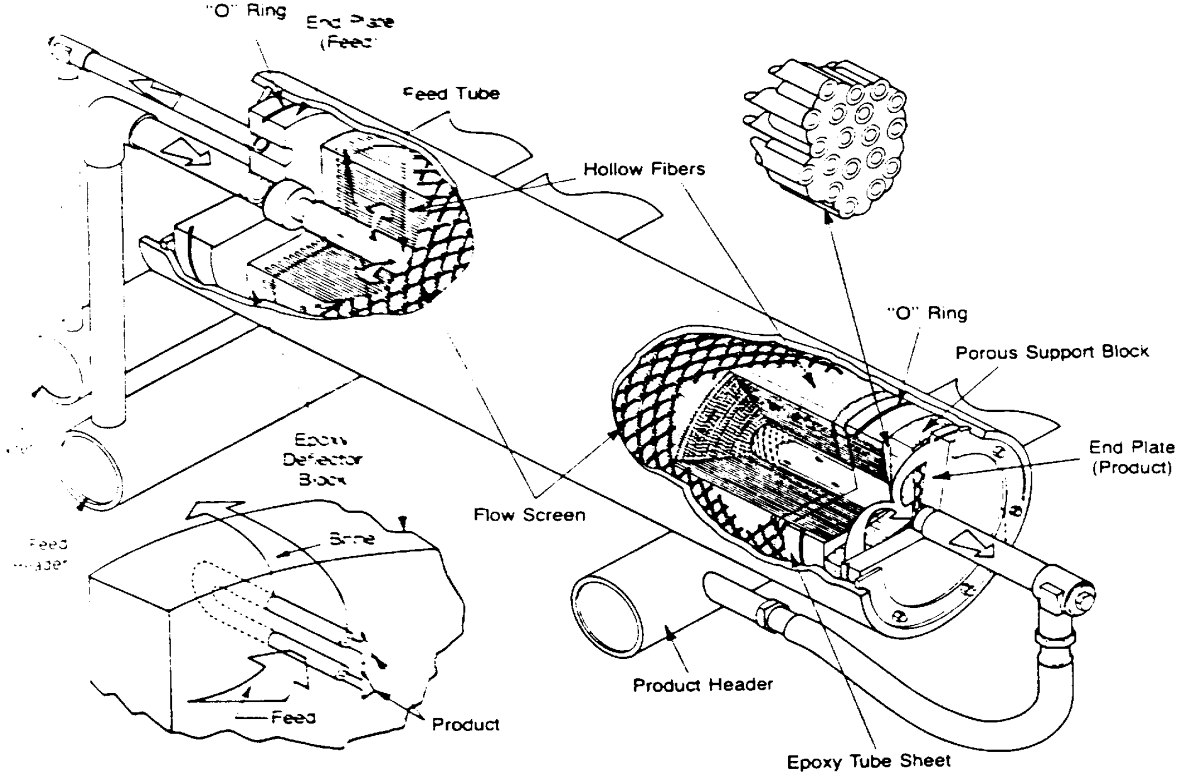


Figure 11.5 Hollow fiber permeator construction and hookup. (*Courtesy of E.I. du Pont de Nemours & Co.*)

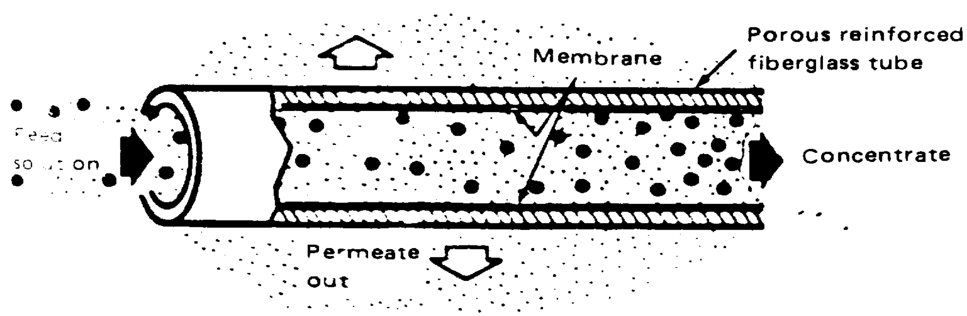


Figure 11.6 Tubular membrane configuration. (*Courtesy of Abcor, Inc.*)

Spiral wound

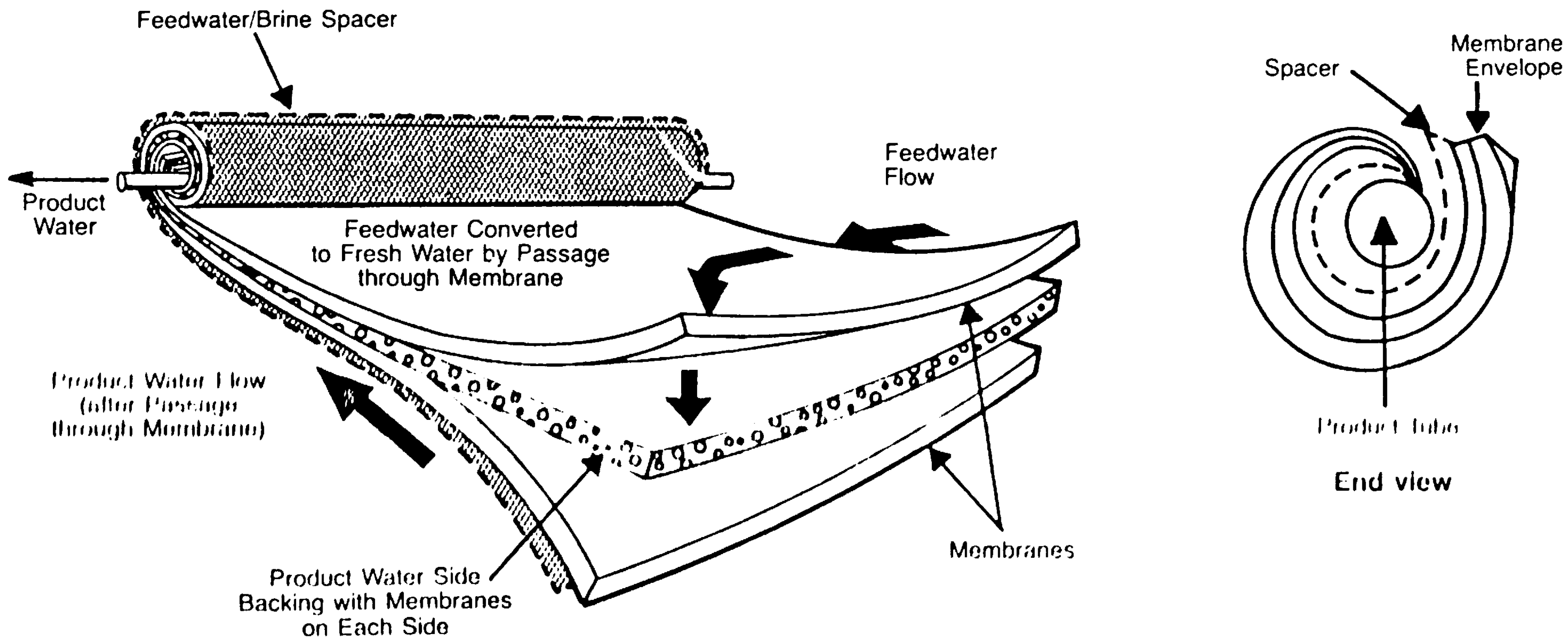
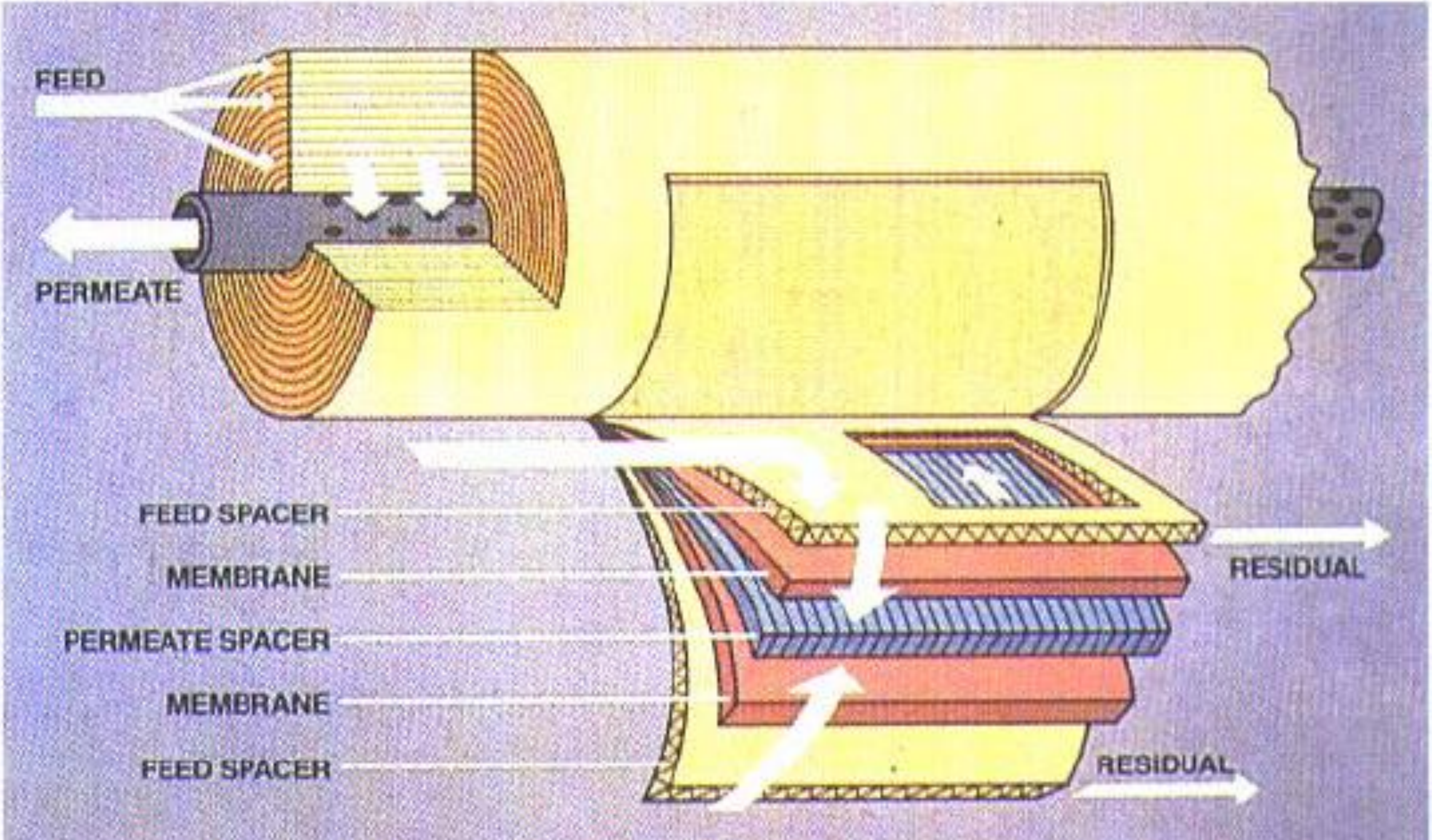
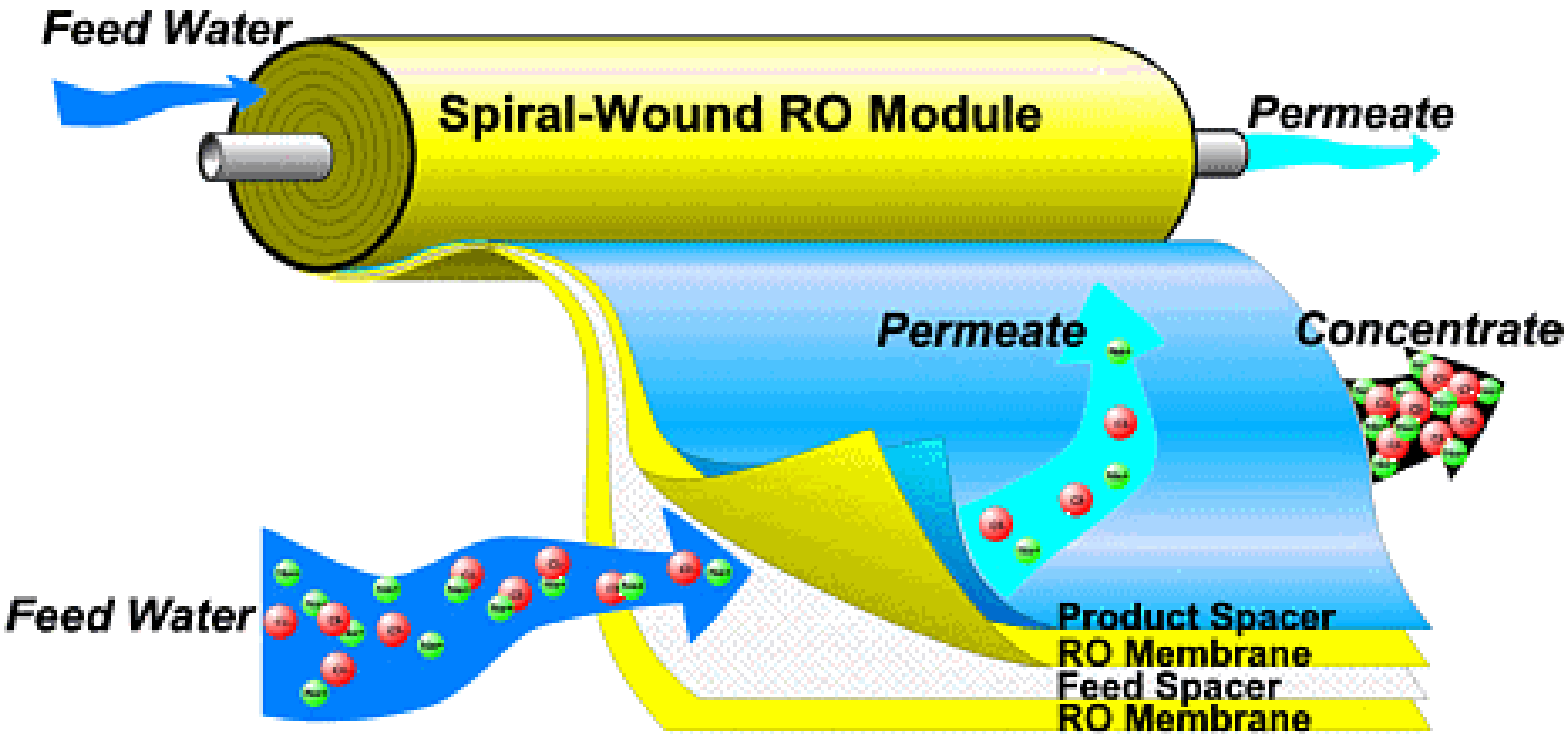


Figure 11.4 Spiral wound reverse-osmosis cartridge. (*Courtesy of E.I. du Pont de Nemours & Co.*)

Spiral-Wound Membrane Element




Feed Water
Spiral-Wound RO Module
Permeate
Permeate
Concentrate
Feed Water
Product Spacer
RO Membrane
Feed Spacer
RO Membrane

Modules

Ceramic Membrane Elements

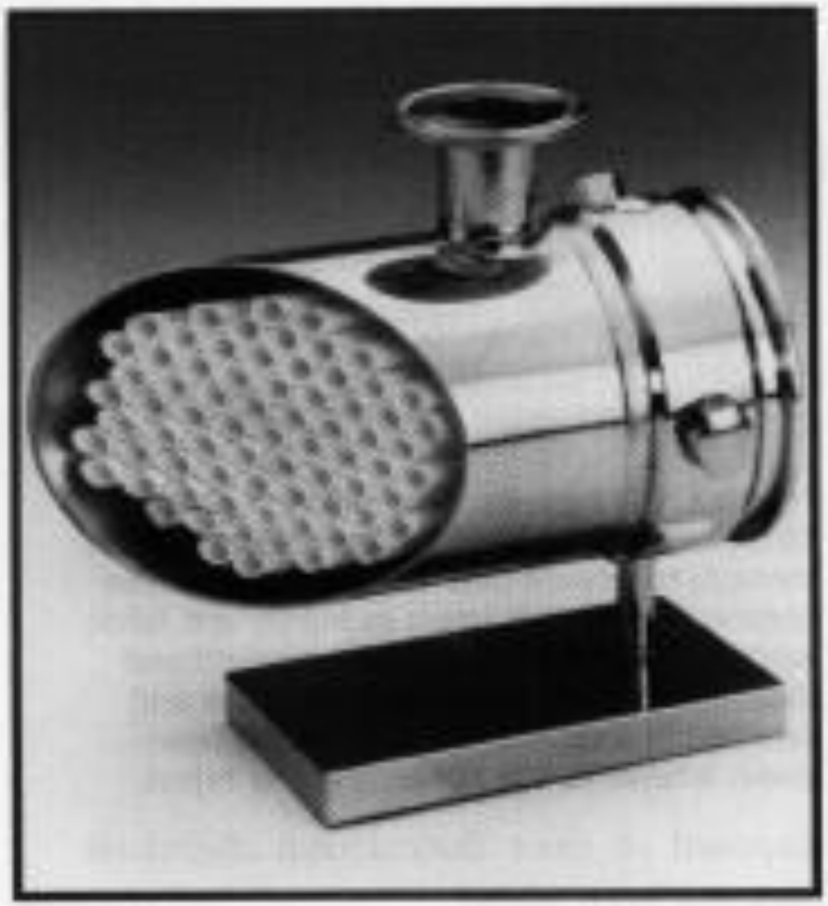


Figure 2. Compact A5 tubular UF modules are made up of a replaceable core of 1/4-inch membrane tubes in a stainless-steel housing. The small diameter tubes require no external support, so the A5 module can provide almost twice the filtration area without increasing overall plant size. The units can handle up to 70 percent suspended solids.

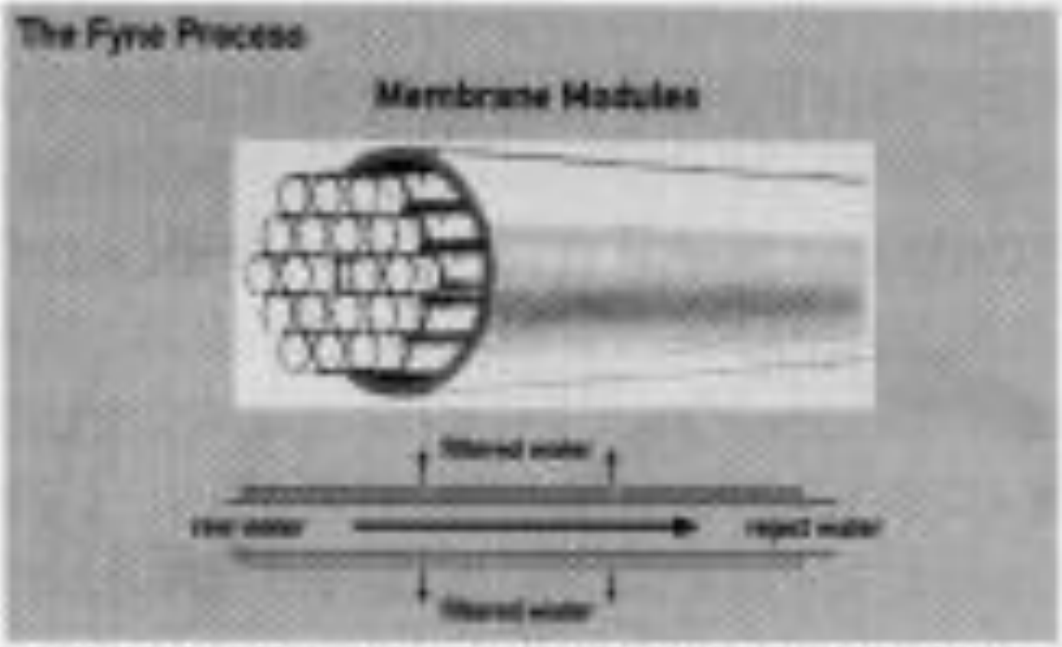


Figure 3. The Fyne Process is based on nanofiltration, which allows inorganic ions to pass through the membrane with the filtrate. The organic compounds (such as humic and fulvic acid) that cause the high color content and disinfection by-products are held back and retained in a small proportion of the raw water known as the concentrate or reject.

disposed of since flocculation chemicals

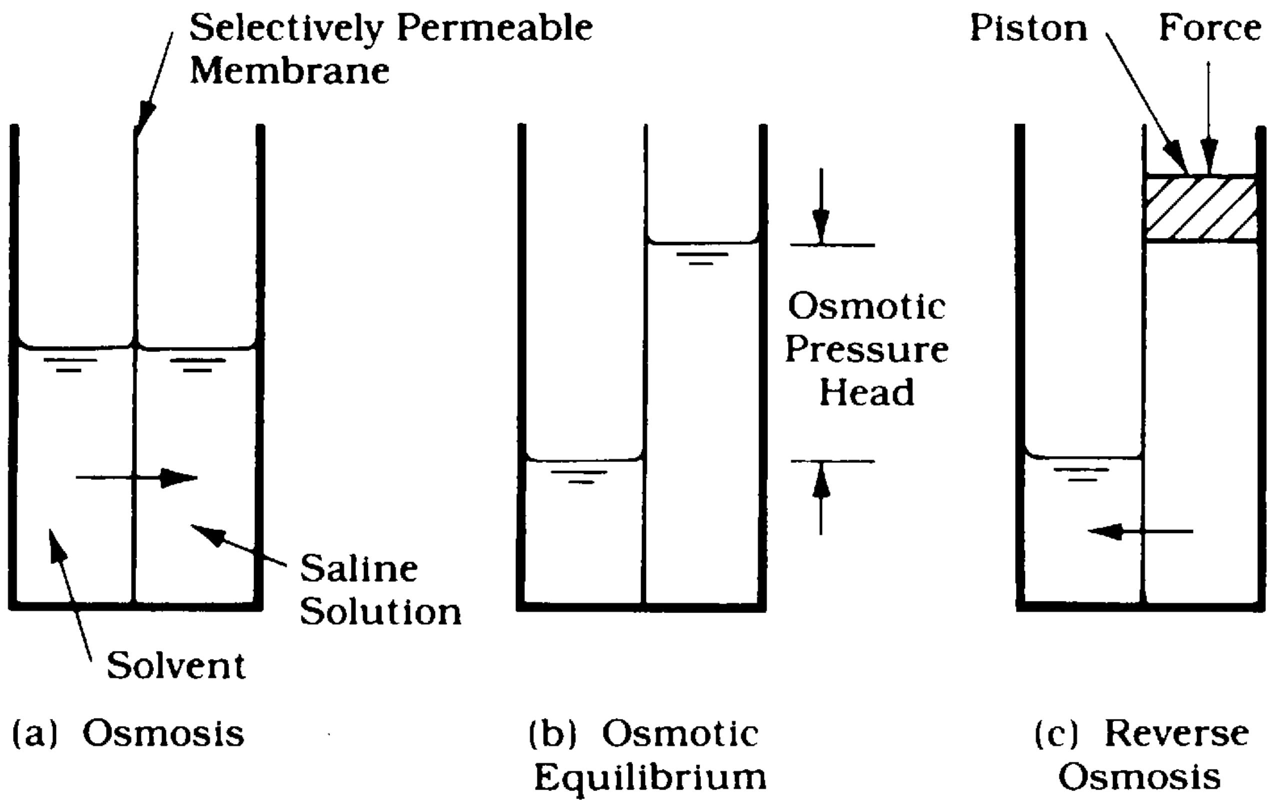
Figure 1. This membrane filtration installation involves two-stage processing of petrochemical plant wastewater. UF unit (left foreground) provides initial separation of particulates and solids, while the spiral membrane reverse-osmosis unit (right background) separates water for re-use and polyol for incineration with the particulate waste.

Spiral UF system

Pressure requirements are based on osmotic pressure for R.O., osmotic pressure and fluid mechanical frictional headloss (straining) for nanofiltration, and purely fluid mechanical frictional headloss (straining) for ultra- and microfiltration.

If clean water and water with some concentration of solute are separated by a semi-permeable membrane (permeable to only water) water will be transported across the membrane until increases hydrostatic pressure on the solute side will force the process to stop.

FIGURE 14.3
Osmosis and Reverse Osmosis



The osmotic pressure head (at equilibrium) can be calculated from thermodynamics.

The chemical potential (Gibbs free energy per mole) of the solvent and the solute(s) in any phase can be described as:

$$\mu_i = \mu_i^0(T,p) + RT \ln X_i$$

Where $\mu_i^0(T,p)$ is the "standard state" free energy of a pure solvent or solute at T and p (usually 25^0C and 1 atm). X_i = mole fraction of solvent or solute.

At equilibrium for the solute and pure solvent system, respectively:

$$\mu(T,p+\pi,X)=\mu^0(T,p)$$

$$\mu^0(T,p+\pi)+RT\ln X=\mu^0(T,p)$$

Because:

$$d\overline{G}=-\overline{S}dT+\overline{V}dp$$

$$\mu^0(T,p+\pi)-\mu^0(T,p)=\int_p^{p+\pi}\overline{v}_0dp$$

$$\int_{p}^{p+\pi} \overline{V}_0 \, dp + RT \ln X = 0$$

$$\overline{V}_0 \pi + RT \ln X = 0$$

After some algebraic manipulation:

$$\pi = R \cdot T \frac{n_2}{V_{total}} = R \cdot T \cdot C$$

$\pi =$ osmotic pressure

Water flux through the membrane is the most important design and operational parameter. Next most important is solute exclusion. Some solute will diffuse (by molecular diffusion) through the membrane because there will be a significant gradient of the solute across the membrane.

Water Flux:

$$F_W = K(\Delta p - \Delta \pi)$$

Solute transport is complicated by the type of ions being transported. Transport is generally modeled by :

$$F_s = B\,(C_1 - C_2)$$

F_s = salt flux (g/cm^2 –sec)

Applications of Micro- and Ultrafiltration:

- Conventional water treatment (replace all processes except disinfection).
- Pretreat water for R.O and nanofiltration.
- Iron/Manganese removal (after oxidation).
- Removal of DBP precursors.

Applications for R.O. and nanofiltration:

- R.O. application mostly desalination.
- Nanofiltration first developed to remove hardness.
- Nanofiltration can be used to remove DBP precursors

Operating pressure ranges:

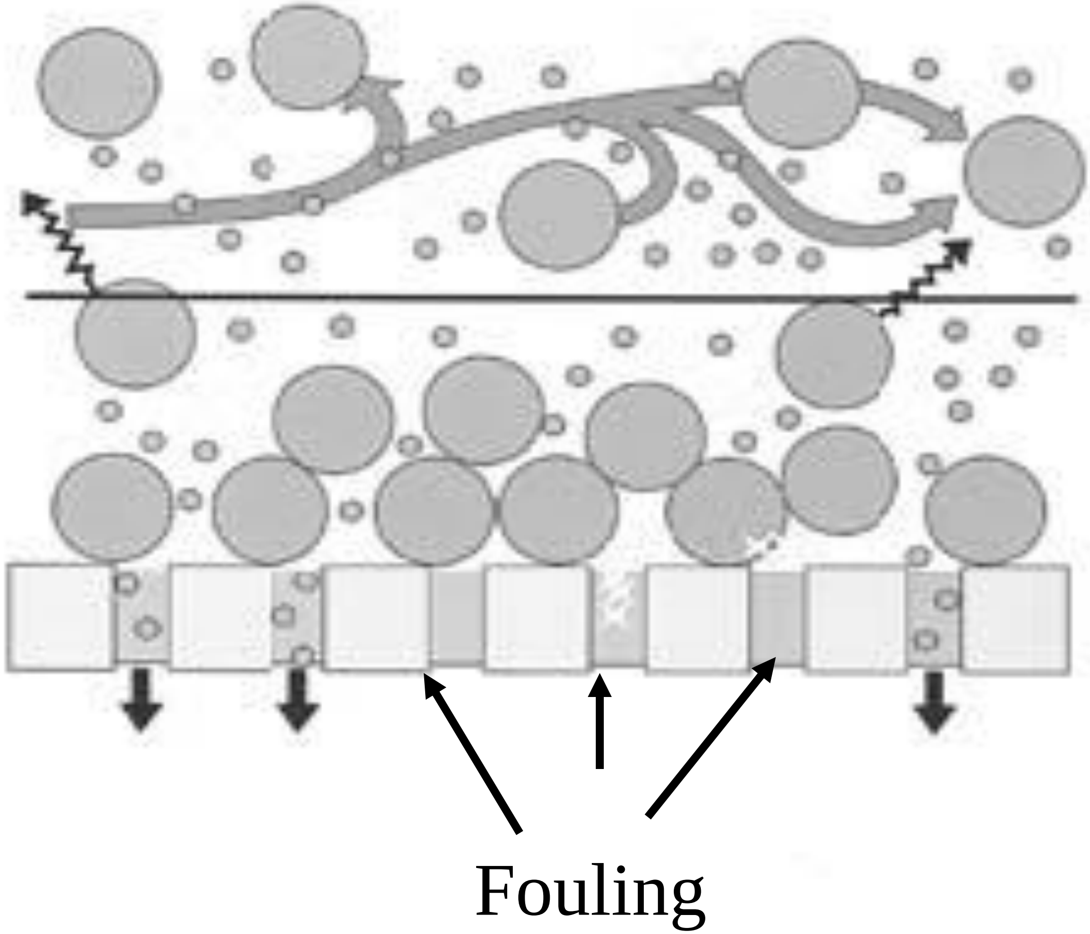
R.O./NF: 80 – 600 psig

MF/UF: 5 – 60 psig

Fouling of membranes due to accumulation of solute/particulates at the membrane interface has to be addressed for economic reasons. The membranes are too expensive to be replaced for reasons of fouling.

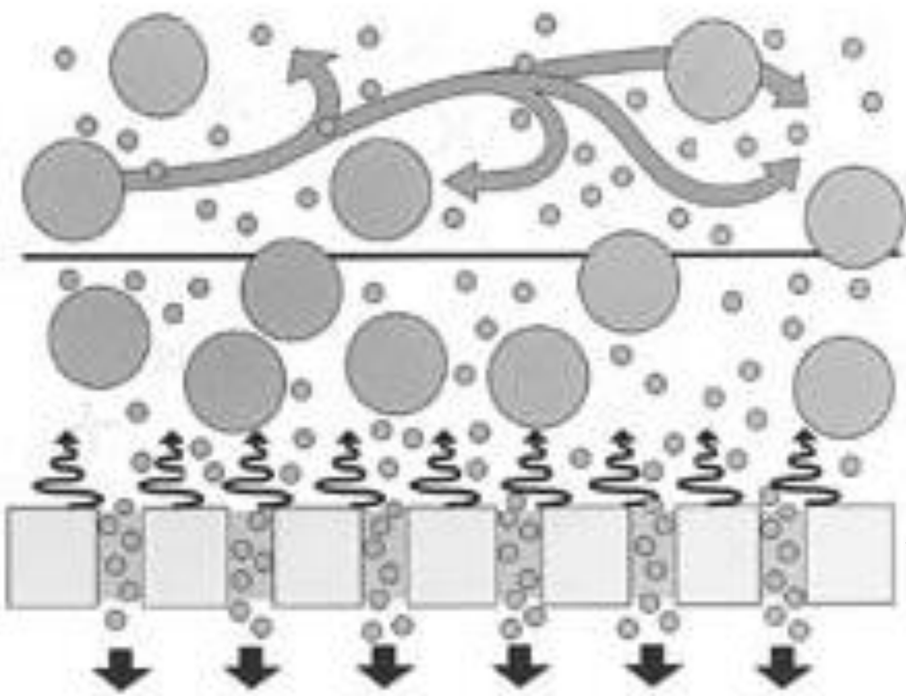
Fouling issue

Traditional membrane technology is generally affected by fouling. This long-term loss in throughput capacity is due primarily to the formation of a boundary layer that builds up naturally on the membrane surface during the filtration process. In addition to cutting down on the flux performance of the membrane, this boundary or gel layer acts as a secondary membrane reducing the native design selectivity of the membrane in use. This inability to handle the buildup of solids has also limited the use of membranes to low-solids feed streams.


Fouling

There are various ways to reduce this fouling such as:

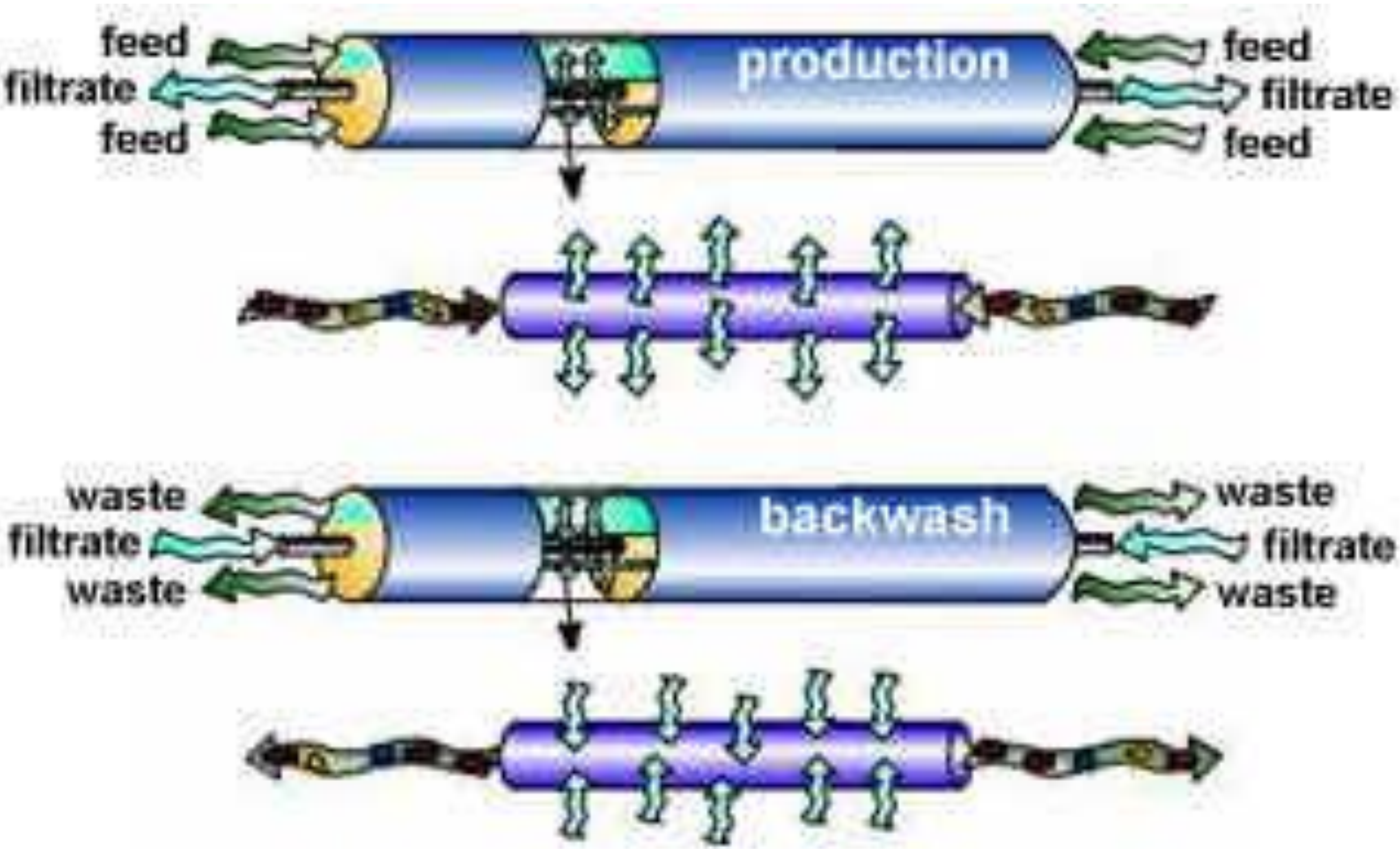
- Periodic pulsing of feed
- Periodic pulsing filtrate (backwashing)
- Increasing shear at by rotating membrane
- Vibrating membrane (VSEP technology , next slide)



Vibrating shear
to prevent fouling

VSEP Technology

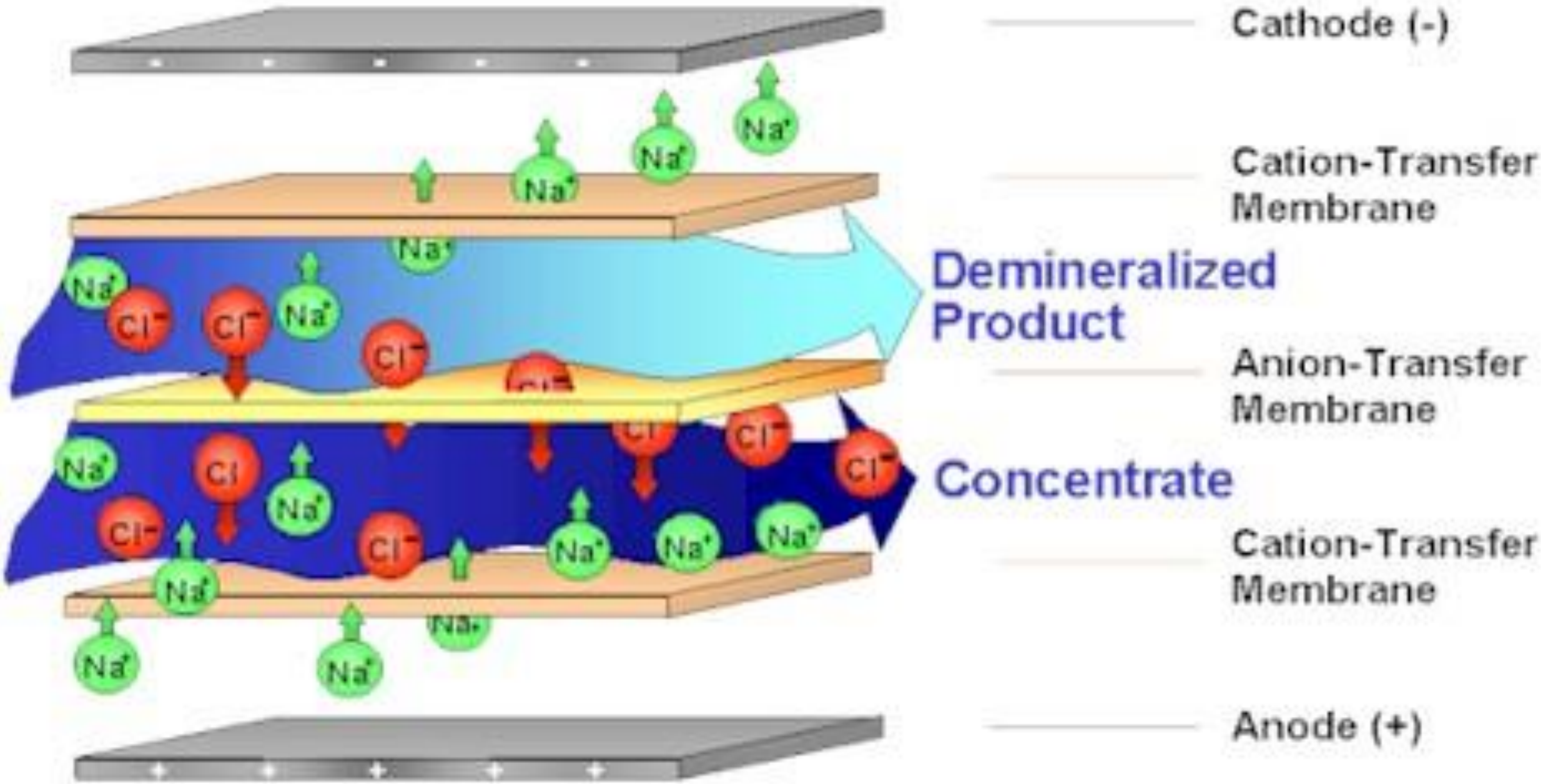
A common method to clean the membrane system is to just reverse the flow pattern:


feed
filtrate
feed
production
feed
filtrate
feed
waste
filtrate
waste
backwash
waste
filtrate
waste

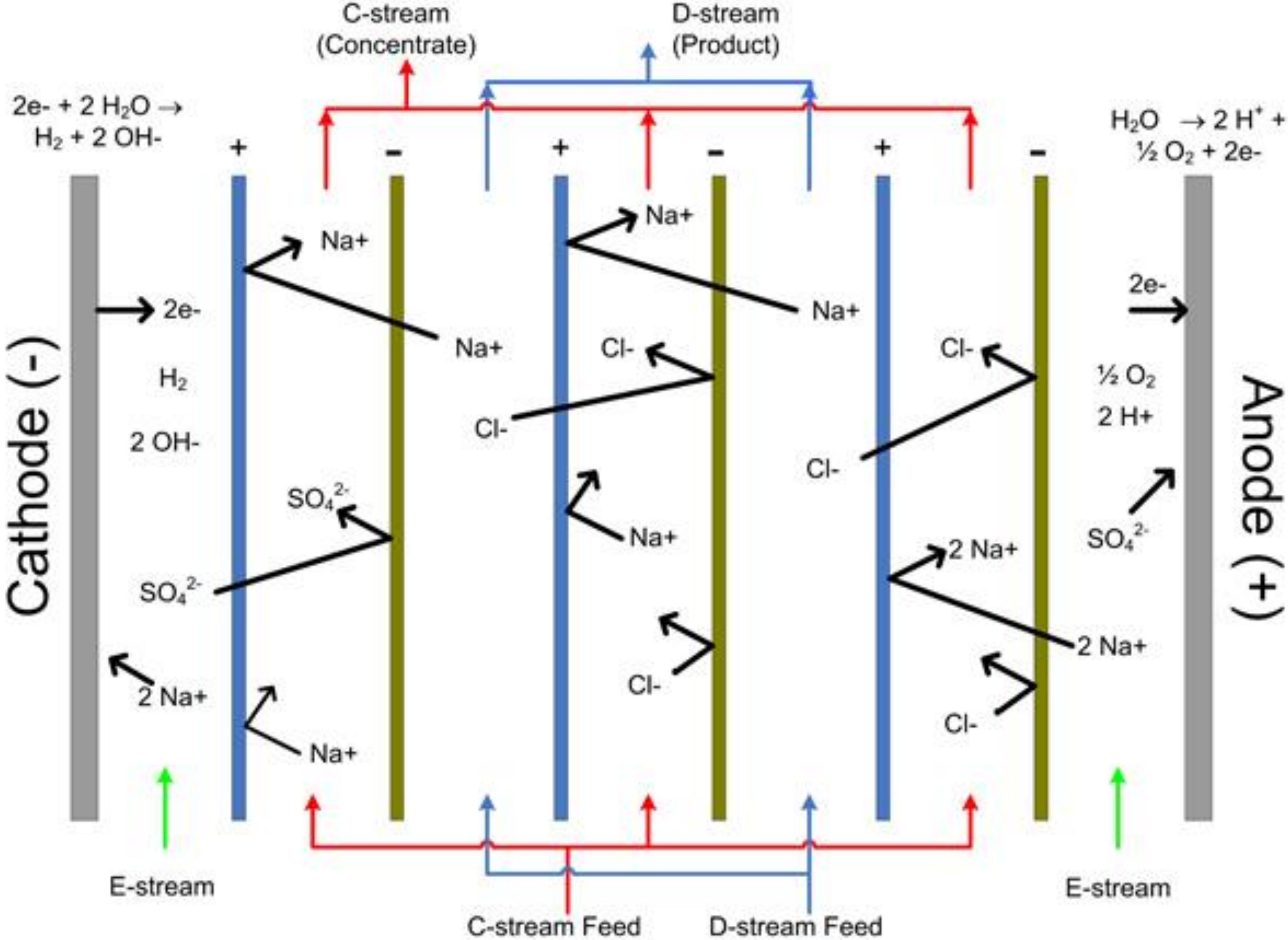
Membrane Processes are becoming popular because they are considered "Green" technology - no chemicals are used in the process.

Electrodialysis:

In the ED process a semi-permeable barrier allows passage of either positively charged ions (cations) or negatively charged ions (anions) while excluding passage of ions of the opposite charge. These semi-permeable barriers are commonly known as ion-exchange, ion-selective or electrodialysis membranes.



Cathode (-)
Cation-Transfer Membrane
Demineralized Product
Anion-Transfer Membrane
Concentrate
Cation-Transfer Membrane
Anode (+)



C-stream
(Concentrate)
D-stream
(Product)
2e- + 2 H₂O →
H₂ + 2 OH-
H₂O → 2 H⁺ +
½ O₂ + 2e-
+
-
+
-
+
-
Na+
Na+
Na+
Na+
2e-
2e-
Cathode (-)
Anode (+)
Cl-
Cl-
H₂
½ O₂
Cl-
2 H+
2 OH-
Cl-
SO₄²⁻
Na+
2 Na+
SO₄²⁻
SO₄²⁻
2 Na+
Cl-
2 Na+
Cl-
Na+
E-stream
E-stream
C-stream Feed
D-stream Feed

Current required in amps:

$$I = \frac{F \cdot Q\left(C_{in} - C_{out}\right)}{n \cdot \xi}$$

$$F = \text{Faraday} = 96{,}485 \frac{\text{amp} \cdot \text{sec}}{\text{equivalent}}$$

$$C_{in,out} = \text{concentration in equiv/m}^3$$

$$\xi = \text{current efficiency (typically 0.8 to 0.9)}$$

n = number of cells

Voltage required is determined by:

$E = I \times R$

R = resistance across unit (all cells + feed and product water), ohms. Generally in range of 10 – 50 ohms.

I, in amps, as determined in previous calculation.

Electrode reactions:

Small amounts of hydrogen gas are generated at the cathode:

$$2e^{-} + 2H_2O \rightarrow H_2(g) + 2OH^{-}$$

At the anode small amounts of oxygen gas are generated:

$$H_2O \rightarrow 2H^{+} + 1/2O_2(g)$$

(also possible $2Cl^{-} \rightarrow Cl_2(g) + 2e^{-}$)