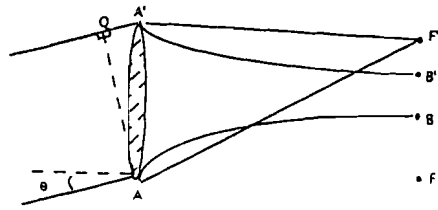


systems in which Gaussian beams are to propagate. For example, a *beam expander*, of which one form is shown in Figure 20.5.33, is an afocal system intended to do what its name implies: if it has aberrations



Lens images point at infinity to F'
 therefore $QA' \cdot A'F' = AF'$ (Fermat)
 $AF' - A'F' = AF' - AF = \text{constant (by property of hyperbola)}$
 $= BB'$
 $QA' = AA' \sin \theta$
 therefore $AA' \sin \theta = BB'$
 $(AA'/BB')^2 = 1/\sin^2 \theta$

FIGURE 20.5.33

as an afocal system, the output beam from a Gaussian input beam will not have truly plane or spherical phase fronts.

Non-Gaussian Beams from Lasers

Not all lasers produce Gaussian beams, even ignoring the inevitable truncation effects of resonator mirrors. Some gas lasers (e.g., helium-neon at any of its lasing wavelengths) produce Gaussian beams when they are in appropriate adjustment, but they can produce off-axis modes with more structure than a Gaussian beam. Other gas lasers (e.g., copper vapor lasers) produce beams with a great many transverse modes covering an angular range of a few milliradians in an output beam perhaps 20 mm across. Some solid-state lasers, e.g., ruby, may produce a very non-Gaussian beam because of optical inhomogeneities in the ruby. Laser diodes, which as already mentioned are becoming increasingly useful as very compact coherent sources, whether cw or pulsed, produce a single strongly divergent transverse mode which is wider across one direction than the other. This mode can be converted into a circular section of approximately Gaussian profile by means of a prism system, as in Figure 20.5.24.

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20.6 Water Desalination

Noam Lior

Introduction and Overview

Water desalination is a process that separates water from a saline water solution. The natural water cycle is the best and most prevalent example of water desalination. Ocean waters evaporate due to solar heating and atmospheric influences; the vapor consisting mostly of fresh water (because of the negligible volatility of the salts at these temperatures) rises buoyantly and condenses into clouds in the cooler atmospheric regions, is transported across the sky by cloud motion, and is eventually deposited back on the earth surface as fresh water rain, snow, and hail. The global freshwater supply from this natural cycle is ample, but many regions on Earth do not receive an adequate share. Population growth, rapidly increasing demand for fresh water, and increasing contamination of the available natural fresh water resources render water desalination increasingly attractive. Water desalination has grown over the last four decades to an output of about 20 million m^3 of fresh water per day, by about 10,000 sizeable land-based water desalination plants.

The salt concentration in the waters being desalted ranges from below 100 ppm wt. (essentially fresh water, when ultrapure water is needed), through several thousand parts per million (brackish waters unsuitable for drinking or agricultural use) and seawater with concentrations between 35,000 and 50,000 ppm. Official salt concentration limits for drinkable water are about 1000 ppm, and characteristic water supplies are restricted to well below 500 ppm, with city water in the United States being typically below 100 ppm. Salinity limits for agricultural irrigation waters depend on the type of plant, cultivation, and soil, but are typically below 2000 ppm.

Many ways are available for separating water from a saline water solution. The oldest and still prevalent desalination process is distillation. The evaporation of the solution is effected by the addition of heat or by lowering of its vapor pressure, and condensation of these vapors on a cold surface produces fresh water. The three dominant distillation processes are multistage flash (MSF), multieffect (ME), and vapor compression (VC). Until the early 1980s the MSF process was prevalent for desalination. Now membrane processes, especially reverse osmosis (RO), are economical enough to have taken about one third of the market. In all membrane processes separation occurs due to the selective nature of the permeability of a membrane, which permits, under the influence of an external driving force, the passage of either water or salt ions but not of both. The driving force may be pressure (as in RO), electric potential (as in electrodialysis, ED), or heat (as in membrane distillation, MD). A process used for low-salinity solutions is the well-known ion exchange (IE), in which salt ions are preferentially adsorbed onto a material that has the required selective adsorption property and thus reduce the salinity of the water in the solution.

The cost of desalted water is comprised of the capital cost of the plant, the cost of the energy needed for the process, and the cost of operation and maintenance staff and supplies. In large seawater desalination plants the cost of water is about \$1.4 to \$2/ m^3 , dropping to less than \$1/ m^3 for desalting brackish water. A methodology for assessing the economic viability of desalination in comparison with other water supply methods is described by Kasper and Lior (1979). Desalination plants are relatively simple to operate, and progress toward advanced controls and automation is gradually reducing operation expenses. The relative effect of the cost of the energy on the cost of the fresh water produced depends on local conditions, and is up to one half of the total.

The boiling point of a salt solution is elevated as the concentration is increased, and the boiling point elevation is a measure of the energy needed for separation. Thermodynamically reversible separation defines the minimal energy requirement for that process. The minimal energy of separation W_{min} in such a process is the change in the Gibbs free energy between the beginning and end of the process, ΔG . The minimal work when the number of moles of the solution changes from n_1 to n_2 is thus

$$W_{min} = \int_{n_1}^{n_2} (\Delta G) dn_w \quad (20.6.1)$$

The minimal energy of separation of water from seawater containing 3.45 wt.% salt, at 25°C, is 2.55 kJ/(kg fresh water) for the case of zero fresh water recovery (infinitesimal concentration change) and 11 kJ/(kg fresh water) for the case of 25% freshwater recovery. W_{min} is, however, severalfold smaller than the energy necessary for water desalination in practice. Improved energy economy can be obtained if desalination plants are integrated with power generation plants (Aschner, 1980). Such dual-purpose plants save energy but also increase the capital cost and complexity of operation.

Two aspects of the basically simple desalination process require special attention. One is the corrosivity of seawater, especially pronounced in the higher-temperature distillation processes, which requires the use of corrosion-resistant expensive materials. Typical materials in use are copper-nickel alloys, stainless steel, titanium, and, at lower temperatures, fiber-reinforced polymers (George et al., 1975). Another aspect is scale formation (Glaser et al., 1980; Heitman, 1990). Salts in saline water, particularly calcium sulfate, magnesium hydroxide, and calcium carbonate, tend to precipitate when a certain temperature and concentration are exceeded. The precipitate, often mixed with dirt entering with seawater and with corrosion products, will gradually plug up pipes, and when depositing on heat transfer surfaces reduces heat transfer rates and thus impairs plant performance. While the ambient-temperature operation of membrane processes reduces scaling, membranes are much more susceptible only to minute amounts of scaling or even dirt, but also to the presence of certain salts and other compounds that reduce their ability to separate salt from water. To reduce corrosion, scaling, and other problems, the water to be desalted is pretreated. The pretreatment consists of filtration, and may include removal of air (deaeration), removal of CO₂ (decarbonation), and selective removal of scale-forming ions (softening). It also includes the addition of chemicals that allow operation at higher temperatures without scale deposition, or which retard scale deposition and/or cause the precipitation of scale which does not adhere to solid surfaces, and that prevent foam formation during the desalination process.

Saline waters, including seawater, contain, besides a variety of inorganic salts, also organic materials and various particles. They differ in composition from site to site, and also change with time due to both natural and person-made causes. Design and operation of desalination plants requires good knowledge of the saline water composition and properties (Fabuss, 1980; Heitman, 1991).

The major water desalination processes that are currently in use or in advanced research stages are briefly described below. Information on detailed modeling can be found in the references.

Distillation Processes

Single-Stage Flash Evaporation (MSF)

Most of the large desalination plants use the MSF process shown schematically in Figure 20.6.1. A portion of an operating plant is shown in Figure 20.6.2. The seawater feed is preheated by internal heat recovery from condensing water vapor during passage through a series of stages, and then heated to its operating temperature by steam generated by an external heat source. The hot seawater then flows as a horizontal surface stream through a series of "stages," created by vertical walls which separate the vapor space of each stage from the others. These walls allow the vapor space of each stage to be maintained at a different pressure, which is gradually decreased along the flow path due to the gradually decreasing temperature in the condenser/seawater-preheater installed above the free stream. The seawater is superheated by a few degrees Celsius relative to the vapor pressure in each stage it enters, and consequently evaporates in each stage along its flow path. The latent heat of the evaporation is supplied by equivalent conduction of the sensible heat of the evaporating water, thus resulting in a gradual lowering of the stream temperature. The evaporation is vigorous, resulting in intensive bubble generation and growth with accompanying stream turbulence, a process known as flash evaporation (Lior and Greif, 1980; Miyatake et al., 1992; 1993). One of the primary advantages of the MSF process is the fact that evaporation occurs

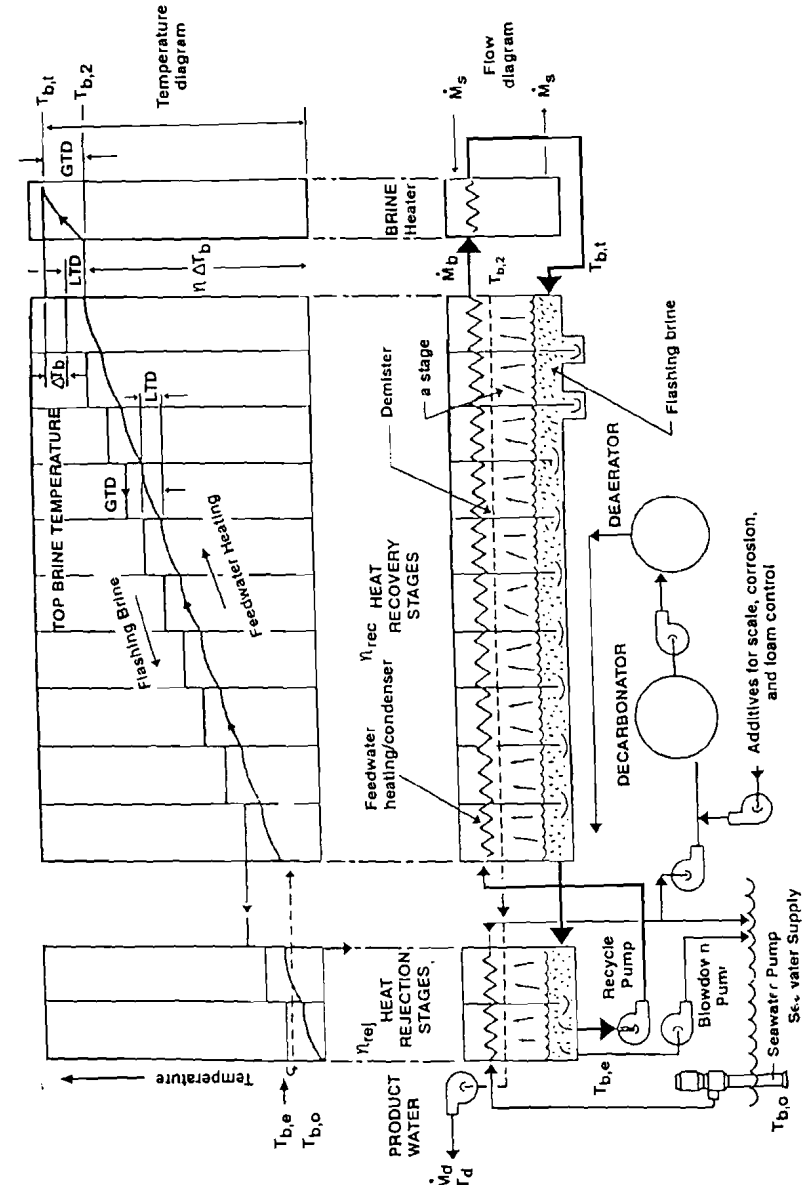


FIGURE 20.6.1 Schematic flow and temperature diagram of the MSF process, for a recirculation type plant.

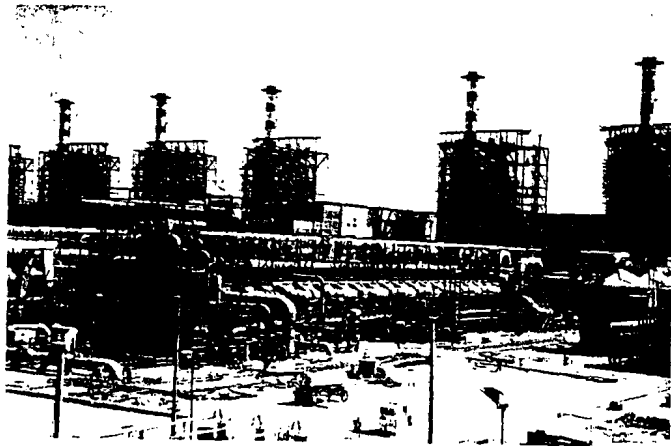


FIGURE 20.6.2 One of the six units of the 346,000 m³/day MSF desalination plant Al Taweelah B in Abu Dhabi, United Arab Emirates. (Courtesy of Italmimpianti S. p. A.) It is a dual-purpose plant, composed of six identical power desalination units. Five of the six boilers are seen in the background. The desalination units were in 1996 the best in the world. They have 17 recovery and 3 reject stages and a performance ratio (PR) of 8.1. The plant also produces 732 MWe of power.

in the saline water stream and not on heated surfaces (as in other distillation processes such as merged tube and ME evaporation) where evaporation typically causes scale deposition and thus dual impairment of heat transfer rates. Also, the fact that the sensible heat of water is much smaller than its latent heat of evaporation, where the specific heat $c_p = 4.182$ kJ/kg/°C change of water temperature the latent heat is $h_{fg} = 2378$ kJ/kg, and the fact that the top temperature is limited by considerations of scaling and corrosion, dictate the requirement for a very large flow rate of the evaporating stream. For example (in the following, the subscripts b , d , and s refer to brine distillate, and steam, respectively), the ratio between a typical top temperature $T_{b,i}$ of 90°C at the inlet to the evaporator and an exit temperature $T_{b,e}$ of 40°C corresponding to the ambient conditions, the overall temperature drop of the evaporating stream is 50°C. By using these values, the heat balance between the sensible heat of the brine stream, flowing at a mass flow rate \dot{m}_b , and the latent heat needed for generating water vapor (distillate) at a mass flow rate \dot{m}_d is

$$(\dot{m}_b - \dot{m}_d)c_p(T_{b,i} - T_{b,e}) = \dot{m}_d h_{fg} \quad (20.6.2)$$

which yields the brine-to-product mass flow ratio as

$$\frac{\dot{m}_b}{\dot{m}_d} = \frac{h_{fg}}{c_p(T_{b,i} - T_{b,e})} + 1 = \frac{2378}{(4.182)(50)} + 1 = 12.37 \quad (20.6.3)$$

Therefore, 12.37 kg of saline water are needed to produce 1 kg of distillate. This high flow rate incurs corresponding pumping equipment and energy expenses, sluggish system dynamics, and, since the stream depth is limited to about 0.3 to 0.5 m for best evaporation rates, also requires large evaporator footprints with their associated expense.

The generated water vapor rises through a screen ("demister") placed to remove entrained saline water droplets. Rising further, it then condenses on the condenser tube bank, and internal heat recovery is

achieved by transferring its heat of condensation to the seawater feed that is thus being preheated. This internal heat recovery is another of the primary advantages of the MSF process. The energy performance of distillation plants is often evaluated by the *performance ratio*, PR, typically defined as

$$PR \equiv \frac{\dot{m}_d}{\dot{m}_s} \quad (20.6.4)$$

where \dot{m}_s is the mass flow rate of heating steam. Since the latent heat of evaporation is almost the same for the distillate and the heating steam, PR is also the ratio of the heat energy needed for producing one unit mass of product (distillate) to the external heat actually used for that purpose. Most of the heating of the brine stream to the top temperature $T_{b,i}$ is by internal heat recovery, and as seen in Figure 20.6.1, the external heat input is only the amount of heat needed to elevate the temperature of the preheated brine from its exit from the hottest stage at $T_{b,1}$ to $T_{b,r}$. Following the notation in Figure 20.6.1, and using heat balances similar to that in Equation (20.6.3) for the brine heater and flash evaporator, the PR can thus also be defined as

$$PR = \frac{\dot{m}_b(\overline{c_{p,b}})_{r \rightarrow i}(T_{b,i} - T_{b,r})/h_{fg,b}}{\dot{m}_h(\overline{c_{p,b}})_{2 \rightarrow 1}(T_{b,1} - T_{b,2})/h_{fg,s}} = \frac{T_{b,i} - T_{b,r}}{T_{b,1} - T_{b,2}} \quad (20.6.5)$$

where $(\overline{c_{p,b}})_{r \rightarrow i}$ and $(\overline{c_{p,b}})_{2 \rightarrow 1}$ are the specific heats of brine, the first averaged over the temperature range $T_{b,r} \rightarrow T_{b,i}$ and the second over $T_{b,2} \rightarrow T_{b,1}$. The rightmost expression in Equation (20.6.5) is nearly correct because the specific heat of the brine does not change much with temperature, and the latent heat of evaporation of the brine is nearly equal to the latent heat of condensation of the heating steam. It is obvious from Equation (20.6.5) that PR increases as the top heat recovery temperature $T_{b,2}$ (at the exit from the condenser/brine-preheater) increases. It is also obvious (even from just examining Figure 20.6.1) that increasing the number of stages (matched with a commensurate increase in condenser heat transfer area and assuming no significant change in the overall heat transfer coefficient) for a given $T_{b,r}$ will raise the flash evaporator inlet temperature $T_{b,1}$, which will lead to a rise in $T_{b,2}$ and thus also in the PR.

Assuming that the temperature drop of the flashing brine, $\Delta T_{b,i}$, is the same in each stage, the relationship between the number of stages (n) and the performance ratio is

$$PR = \frac{1}{\frac{\text{LTD}}{T_{b,i} - T_{b,r}} + \frac{1}{n}} \quad (20.6.6)$$

where LTD is the lowest temperature difference between the flashed vapor and the heated feedwater, in each stage (Figure 20.6.1). Equation (20.6.6) shows that increasing the number of stages increases the PR. This implies that more heat is then recovered internally, which would thus require a larger condenser/brine-preheater heat transfer area. The required heat transfer area, A , per unit mass of distillate produced for the entire heat recovery section (composed of n_{rec} stages), and taking average values of the overall vapor-to-feedwater heat transfer coefficient U and LMTD, is thus

$$A = n_{\text{rec}} A_n = n_{\text{rec}} \frac{h_{b,r}}{U(\text{LMTD})} \quad (20.6.7)$$

LMTD, the log-mean temperature difference between the vapor condensing on the tubes and the heated brine flowing inside the tubes, for an average stage is

$$\text{LMTD} = \frac{\text{GTD} - \text{LTD}}{\ln \frac{\text{GTD}}{\text{LTD}}} = \frac{(T_{b,1} - T_{b,2}) - \text{LTD}}{\ln \left(\frac{T_{b,1} - T_{b,2}}{\text{LTD}} \right)} \quad (20.6.8)$$

where GTD is the greatest temperature difference between the flashing brine and the brine heated in the condenser. The size of the heat transfer area per unit mass of distillate is

$$A = \frac{h_{f,b}}{U} \frac{n_{\text{rec}}}{(T_{b,1} - T_{b,e})} \ln \left(\frac{n_{\text{rec}}}{n_{\text{rec}} - PR} \right) \quad (20.6.9)$$

Examination of this equation will show that the required heat transfer area for the heat recovery section per unit mass of distillate produced, A , increases significantly when PR is increased, and decreases slightly as the number of heat recovery stages, n_{rec} , is increased.

The MSF plant shown in Figure 20.6.1 is of the *recirculation* type, where not all of the brine stream emerging from the last evaporation stage is discharged from the plant (as it would have been in a *once-through* type of plant). A fraction of the emerging brine is mixed with pretreated seawater and recirculated to the condenser of the heat recovery section of the plant. Since only a fraction of the entire stream is new seawater, which needs to be pretreated (removal of air and CO_2 , i.e., deaeration and decarbonation, and the addition of chemicals that reduce scale deposition, corrosion, and foaming), the overall process cost is reduced. The recirculation plant is also easier to control than the once-through type.

While most of the energy exchange in the plant is internal, steady-state operation requires that energy in an amount equal to all external energy input be also discharged from the plant. Consequently, the amount supplied in the brine heater (plus any pumping energy) is discharged in the heat rejection stages of the plant (Figure 20.6.1). Assuming an equal temperature drop in each stage, and that the pumping energy can be neglected relative to the heat input in the brine heater, indicates that the ratio of the number of the heat-recovery to heat-rejection stages is approximately equal to the performance ratio PR .

Further detail about MSF desalination can be found in Steinbruechel and Rhinesmith, (1980) and Khan (1986). A detailed design of an MSF plant producing 2.5 million gals. of freshwater per day was published by the U.S. government (Burns and Roe, 1969).

Multi-Effect Distillation (ME)

The principle of the ME distillation process is that the latent heat of condensation of the vapor generated in one effect is used to generate vapor in the next effect, thus obtaining internal heat recovery and good energy efficiency. Several ME plant configurations, most prominently the horizontal tube ME (HTME, shown in Figure 20.6.3) and the vertical tube evaporator (VTE, shown schematically in Figure 20.6.4) are in use. In the HTME, vapor is circulated through a horizontal tube bundle, which is subjected to an internal spray of somewhat colder saline water. The vapor flowing in these spray-cooled tubes condenses, the latent heat of condensation is transferred through the tube wall to the saline water spray striking the exterior of the tube, causing it to evaporate. The vapor generated thereby flows into the tubes in the next effect, and the process is repeated from effect to effect.

In the VTE the saline water typically flows downward inside vertical tubes and evaporates as a result of the condensation of vapor coming from a higher temperature effect on the tube exterior. While internal heat recovery is a feature common to both MSF and ME processes, there are at least three important differences between them. One is that evaporation in the ME process occurs on the heat transfer surfaces (tubes), while in the MSF process it takes place in the free stream. This makes the ME process much less susceptible to scale formation. At the same time, the heat transfer coefficient between the vapor and the preheated brine is lower in the MSF process because the heated brine does not boil. In the ME

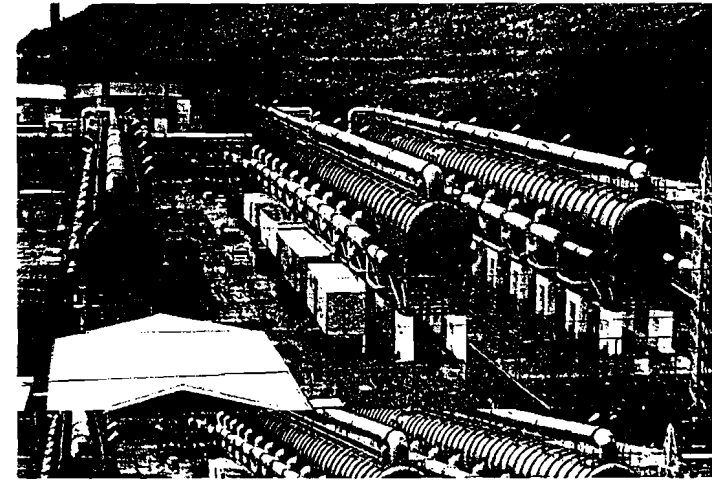


FIGURE 20.6.3 Two HTME desalination units, each producing 5000 m³/day, in St. Croix, U.S. Virgin Islands. (Courtesy of I.D.E. Technologies Ltd.)

process it does boil, and it is well known that boiling heat transfer coefficients are significantly higher than those where the heating does not result in boiling. In using direct transfer of latent heat of condensation to latent heat of evaporation, instead of sensible heat reduction to latent heat of evaporation as in MSF, the ME process requires a much smaller brine flow than the MSF. Limiting brine concentration in the last effect to about three times that of the entering seawater, for example, requires a brine flow of only about 1.5 times that of the distillate produced. At the same time, a pump (although much smaller than the two pumps needed in MSF) is needed for each effect.

The PR of ME plants is just slightly lower than the number of effects, which is determined as an optimized compromise between energy efficiency and capital cost. Six effects are typical, although plants with as many as 18 effects have been built.

Further detail about ME desalination can be found in Steinbruechel and Rhinesmith (1980) and Standiford, (1986a).

Vapor Compression Distillation (VC)

As stated earlier, the vapor pressure of saline water is lower than that of pure water at the same temperature, with the pressure difference proportional to the boiling point elevation of the saline water. Desalination is attained here by evaporating the saline water and condensing the vapor on the pure water. Therefore, the pressure of the saline water vapor must be raised by the magnitude of that pressure difference, plus some additional amount to compensate for various losses. This is the principle of the vapor compression desalination method. Furthermore, as shown in Figure 20.6.5, the heat of condensation of the compressed vapor is recovered internally by using it to evaporate the saline water. Additional heat recovery is obtained by transferring heat from the concentrated brine effluent and the produced freshwater (which need to be cooled down to as close to ambient conditions as possible anyway) to the feed saline water which is thus preheated. The schematic flow diagram in Figure 20.5.5 shows a design in which the preheated seawater is sprayed onto a bank of horizontal tubes carrying condensing compressed vapor at a temperature higher than that of the seawater. The spray thus evaporates on contact with the exterior of the tube and provides the cooling needed for the internal condensation. Considering the fact that the energy required for vapor compression over a typical overall temperature difference of 4°C and a vapor compressor efficiency of 0.8 is 34 kJ/kg (easily calculated from an enthalpy balance), and that the latent

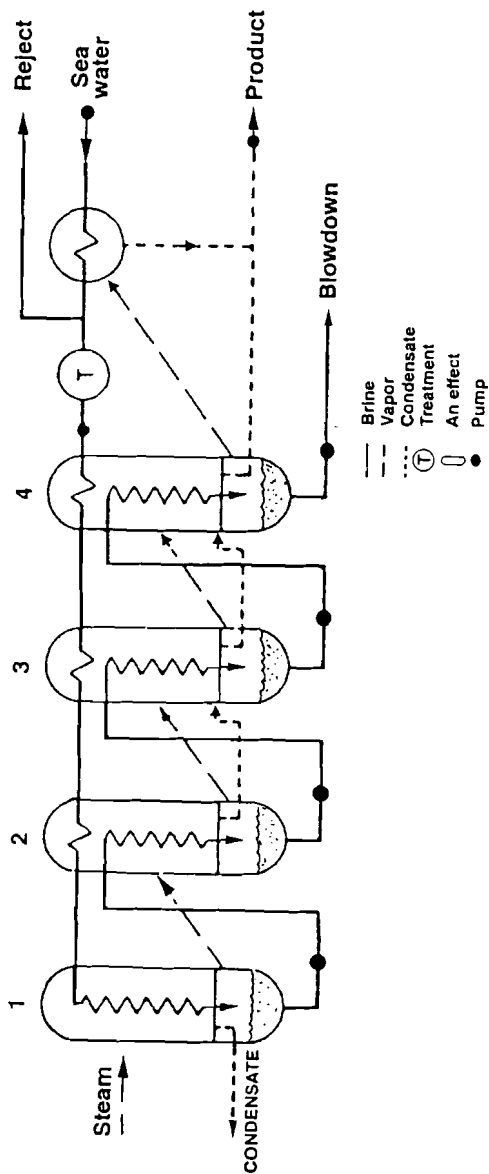


FIGURE 20.6.4 Simplified schematic flow diagram of a typical four-effect VTE desalination plant.

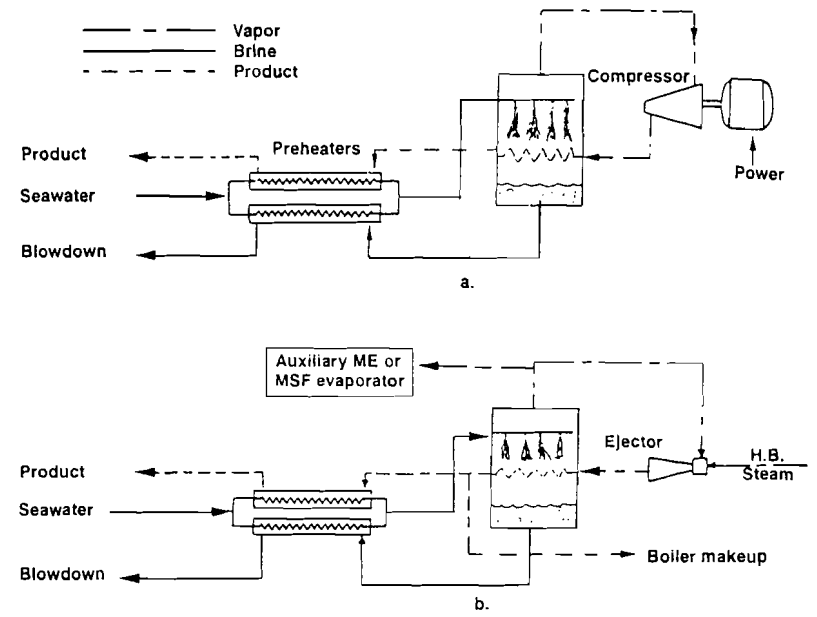


FIGURE 20.6.5 Schematic flow diagram of a basic horizontal-tube VC desalination plant (a) with mechanical, motor-driven compressor; (b) with a thermo-compressor, using an ejector.

heat of condensation is about 2400 kJ/kg, one can see that a small amount of compression energy enables a large amount of heat to be used internally for desalination. One can thus envisage the VC plant as a large flywheel, wheeling a large amount of energy around at the expense of a small amount needed for sustaining its motion.

The compressor can be driven by electric motors, gas or steam turbines, or internal combustion (usually diesel) engines. The compressor can also be a steam-driven ejector (Figure 20.6.5b), which improves plant reliability because of its simplicity and absence of moving parts, but also reduces its efficiency because an ejector is less efficient than a mechanical compressor. In all of the mentioned thermally driven devices, turbines, engines, and the ejector, the exhaust heat can be used for process efficiency improvement, or for desalination by an additional distillation plant.

Figure 20.6.6 shows a multi-effect VC plant. Using more than a single effect reduces the vapor volume that needs to be compressed. Furthermore, the overall required heat transfer area is also decreased because much of the single-phase heat transfer process in the preheater of the single-effect plant is replaced by the high-heat-transfer condensation–evaporation processes in the effects. Although the ME feature also increases the required compression ratio, the cost of produced water is reduced overall.

Further detail about VC desalination can be found in Steinbruchel and Rhinesmith (1980), Khan (1986), and Standiford, (1986b).

Solar Distillation

The benefits of using the nonpolluting and practically inexhaustible energy of the sun for water desalination are obvious. Furthermore, many water-poor regions also have a relatively high solar flux over a large fraction of the time. The major impediment in the use of solar energy is economical: the diffuse nature of solar energy dictates the need for constructing a large solar energy collection area. For example,

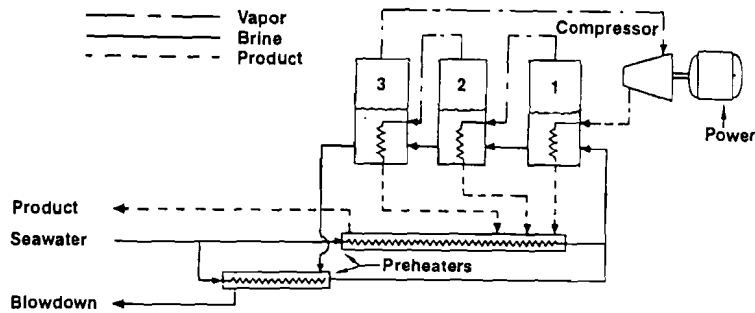


FIGURE 20.6.6 Schematic flow diagram of a ME vapor compression submerged-tube desalination plant with three effects.

Assuming a single-effect solar still efficiency of 50% (which is the upper practical limit for conventional designs), the still would produce at most about 3.5 to 4.8 kg fresh water per m^2 per day, or a 208 to 286 solar still would be required to produce $1 m^3$ of fresh water per day. More realistic still efficiencies increase the area requirement about twofold.

As shown in Figure 20.6.7, a typical solar still consists of a saline water container in which the water is exposed to the sun and heated by it. The temperature rise to above ambient causes net evaporation of saline water, thus separating pure water vapor from the solution. The vapor condenses on the colder cover, and this distilled water flows to collection troughs.

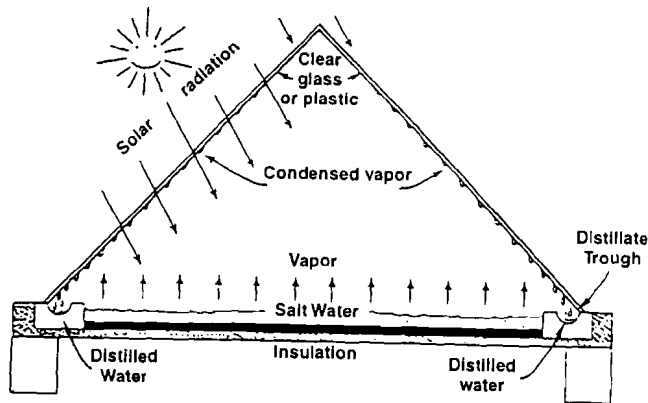


FIGURE 20.6.7 A typical basin-type solar still.

Solar stills of the type depicted in Figure 20.6.7, in many sizes and constructional variants, have been used successfully in many countries in the world. They are simple, easy to construct, reliable, require very little maintenance although in some regions the covers must be cleaned frequently from mulated dust or sand.

Since the heat of condensation in single-effect stills of the type shown in Figure 20.6.7 is lost to the ambient, more-energy-efficient operation can obviously be achieved in a multi-effect design, where the

heat of condensation is used to evaporate additional saline water. A number of such stills were built and tested successfully, but are not commercially competitive yet.

Solar stills integrate the desalination and solar energy collection processes. Another approach to solar desalination is to use separately a conventional desalination process and a suitable solar energy supply system for it. Any compatible desalination and solar energy collection processes could be used. Distillation, such as MSF or ME, can be used with heat input from solar collectors, concentrators, or solar ponds (Hoffman, 1992; Glueckstern, 1995). Net average solar energy conversion efficiencies of solar collectors (Rabl, 1985; Lior, 1991) are about 25% and of solar ponds (Lior, 1993) about 18%, similar to the efficiencies of solar stills, but the MSF or ME plants can operate at performance ratios of 10 or more, thus basically increasing the freshwater production rate by at least tenfold, or reducing the required solar collection area by at least tenfold for the same production rate.

Solar or wind energy can also be used for desalination processes that are driven by mechanical or electrical power, such as VC, RO, and ED. The solar energy can be used to generate the required power by a variety of means, or photovoltaic cells can be used to convert solar energy to electricity directly.

Freeze Desalination

It is rather well known that freezing of saline water solutions is an effective separation process in that it generates ice crystals that are essentially salt-free water, surrounded by saline water of higher concentration. This process requires much less energy than distillation, and the problems of corrosion and scaling are markedly reduced due to the much lower operating temperatures. Several pilot plants were constructed and have proven concept viability. Nevertheless, the process has not yet reached commercial introduction for several reasons, such as the difficulty in developing efficient and economical compressors for vapor with the extremely high specific volume at the low process pressure, and difficulties in maintaining the vacuum system leak free and in effecting reliable washing of the ice crystals. A review of freeze desalination processes is given by Tleimat (1980).

Membrane Separation Processes

Reverse Osmosis (RO)

Separation of particulate matter from a liquid by applying pressure to the liquid and passing it through a porous membrane, whereby particles larger than the pore size remain on the upstream side of the membrane and the liquid flows to its downstream side, is well known as *filtration*. Semipermeable very dense membranes that actually separate salt molecules (ions) from the water, by similarly keeping the salt on the upstream side and allowing the pressurized pure water to flow through the membrane, were developed in the 1950s. The reverse of this process, osmosis, is well known: for example, if a membrane is placed to separate water from an aqueous salt solution, and the membrane is semipermeable (here meaning that it permits transfer of water only, not the salt components in the aqueous solution), the water will tend naturally to migrate through this membrane into the salt solution. Osmosis is, for example, the major mass transport phenomenon across living cells. The driving force for this water flux is proportional to the concentration difference between the two sides of the membrane, and is exhibited as the so-called osmotic pressure, which is higher by 2.51 MPa on the water side of the membrane for typical seawater at 25°C. If a pressure higher than the osmotic pressure is applied on the saline solution side of the membrane, the water flux can be reversed to move pure water across the membrane from the saline solution side to the pure water one. This process is called *reverse osmosis* (and sometimes *hyperfiltration*), and is the basic principle of RO desalination.

Unlike filtration of particulates, the selective "filtration" of the water in RO is not due to the relationship of the membrane pore size to the relative sizes of the salt and water molecules. Rather, one way to explain the process is that the very thin active surface layer of the membrane forms hydrogen bonds with water molecules and thus makes them unavailable for dissolving salt. Salt thus cannot penetrate through that layer. Water molecules approaching that layer are, however, transported through it by forming

uch hydrogen bonds with it and in that process displacing water molecules that were previously hydrogen bonded at these sites. The displaced water molecules then move by capillary action through the pores of the remainder of the membrane, emerging at its other side.

The most prevalent membrane configurations used in RO plants are of the spiral-wound or hollow-fiber types. The basic spiral-wound-type module (Figure 20.6.8) is made of two sheets placed upon each other and rolled together in an increasing diameter spiral around a cylindrical perforated tube. One of the sheets is in the form of a sandwich typically composed of five layers bonded together along three edges. The two outer layers are the semipermeable membranes. Each of them is backed by a porous material layer for mechanical strength, and the very central layer is a thicker porous material layer that makes up the produced fresh water. The second sheet is a porous mesh through which the high-pressure saline water feed is passed in an axial direction. Product water separates from the saline solution and permeates through the two adjacent semipermeable membranes into the central product water-carrying layer, which conducts it spirally to the unbonded edge of the "sandwich" and to the inner perforated tube. The semipermeable membranes are typically made from cellulose acetate, and more recently from composites of several polymers.

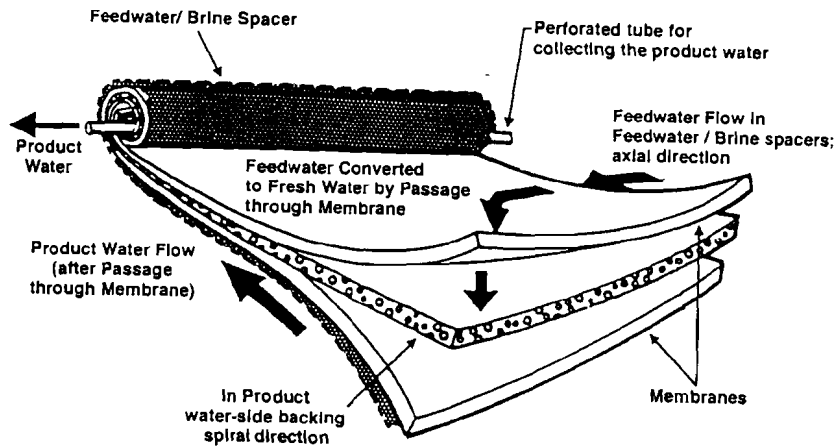


FIGURE 20.6.8 A spiral-wound RO membrane element.

Hollow fiber modules have a configuration similar to a shell-and-tube heat exchanger, with the fibers taking the place of the tubes. A very large number of typically 25 to 250 μm outside-diameter semipermeable hollow fibers (wall thickness typically 5 to 50 μm) are bundled together and placed in a saline water pressure vessel. The hollow core of each fiber is sealed on one end. The pressurized saline water is brought into the module (through a central porous feed tube, Figure 20.6.9) to circulate on the exterior face of the fibers, and water permeates through the fiber wall into its hollow core, through which it flows to a permeate collection manifold at the open end of the fiber bundle. The increasingly concentrated saline water flows radially and is discharged at the exterior shell of the bundle. The hollow fibers are typically made of polyamide or cellulose triacetate, and offer about 20 fold more surface (separation) per unit volume than the spiral-wound configuration.

The basic approximate equation for the separation process gives the water flux \dot{m}_w'' ($\text{kg}/\text{m}^2\text{sec}$) across RO membrane, in the absence of fouling, as

$$\dot{m}_w'' = K_{pe} K_{ct} [(P_f - P_p) - (\pi_f - \pi_p)] \quad (20.6.10)$$

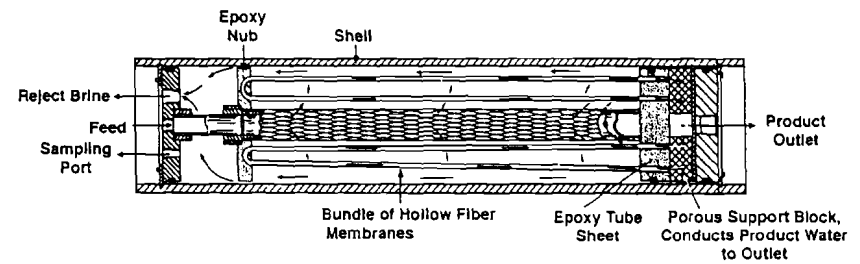


FIGURE 20.6.9 A hollow-fiber RO membrane module. (Du Pont Permasep™.)

where

K_{pe} water permeability constant of the membrane (in $\text{kg}/\text{m}^2\text{sec Pa}$), typically increasing strongly as the temperature rises: a plant designed to operate at 20°C may produce up to 24% more water if the water temperature is 28°C,

K_{ct} compaction correction factor (dimensionless) which corrects for the fact that the flux is reduced due to densification of the barrier layer (a phenomenon similar to creep) of the membrane, and which increases with the operating pressure and temperature. It is often calculated by the relationship

$$K_{ct} = BC(T)C(P)C(t) \quad (20.6.11)$$

where B is a constant,

$C(T)$ represents the temperature dependence of the Compaction Correction Factor for the particular membrane of interest,

$C(P)$ represents its pressure dependence: while a higher pressure difference across the membrane is shown in Equation (20.6.10) to increase the water flux, higher feed pressure (P_f) also tends to compact the membrane and thus reduce its water flux, typically according to

$$C(P) = P_f^n \quad (20.6.12)$$

where n is a negative number,

and where the time dependence $C(t)$ is represented by

$$C(t) = t^m \quad (20.6.13)$$

where t is the operating time (say, in days) and m is a negative number depending on the membrane.

P water or saline solution pressure (Pa),

π osmotic pressure (Pa),

and the subscripts f and p pertain to the saline feed water and to the desalted product water, respectively.

The required membrane area A can be estimated by

$$A = \frac{\dot{m}_p}{\dot{m}_p''} \quad (20.6.14)$$

where \dot{m}_p is the freshwater mass production rate of the plant (kg/sec), and f ($0 < f \leq 1.0$) is the *area utilization factor* that corrects for the fact that the membrane surface is incompletely in contact with the line water feed stream due to the porous mesh and other devices, such as turbulence promoters, placed the feed stream path; in a good design $f > 0.9$.

Examination of Equation (20.6.10) shows that water separation rate increases with the water permeability constant K_{pw} . Unfortunately, so does the salt flux across the membrane, resulting in a saltier product. An approximation for this salt flow is

$$\dot{m}_s = KK_s(C_{fm} - C_p) \quad (20.6.15)$$

where

- \dot{m}_s , salt mass transfer rate across the membrane, kg/sec,
- K , a proportionality constant, dimensionless,
- K_s , salt permeation constant, kg/sec, which increases with pressure and temperature.

The salinity of the product water (C_p) can be estimated by the formula

$$C_p = K_{cp}(1 - \eta)\bar{C} \quad (20.6.16)$$

where

- K_{cp} , concentration polarization coefficient, $\equiv C_{fm}/\bar{C}$ is a measure of the increase of the feedwater salinity at the membrane wall beyond that of the bulk solution,
- \bar{C} , salt concentration at the membrane wall,
- bulk salinity of the saline water feed, $= (C_f + C_r)/2$,
- salt concentration of the reject brine,
- η , salt rejection factor, \equiv (amount of salts rejected by the membrane)/(amount of salts in the brine feed).

The pressure to be used for RO depends on the salinity of the feed water, the type of membrane, and desired product purity. It ranges from about 1.5 MPa for low feed concentrations or high-flux membranes, through 2.5 to 4 MPa for brackish waters, and to 6 to 8.4 MPa for seawater desalination. Desalination of brackish water, typical product water fluxes through spiral-wound membranes are about 600 to 800 kg/(m²day) at a recovery ratio (RR) of 15% and an average salt rejection of 99.5%, where

$$RR = \frac{\dot{m}_p}{\dot{m}_f} \equiv 1 - \frac{C_f}{C_r} \quad (20.6.17)$$

The fluxes in hollow-fiber membranes used in seawater desalination are 20- to 30-fold smaller, but overall RO system size does not increase, because the hollow-fiber membranes have a much larger face area per unit volume. The RR and salt rejection ratio are similar to those of spiral-wound membranes.

Since the concentrated reject brine is still at high pressure, it is possible to recover energy by passing brine through hydraulic turbines, and thus reduce the overall energy consumption by up to 20%. Energy requirements of seawater RO desalination plants with energy recovery are about 5 to 9 kWh, or 8 to 33 MJ, of mechanical or electric power per m³ fresh water produced. In comparison, the MSF desalination process requires about 120 to 280 MJ of heat and about 15 MJ of mechanical/electric power (pumping and auxiliaries) per m³. The energy requirement of the RO process is thus smaller than of the MSF process even if the RO energy requirement is multiplied by the thermal-to-mechanical

(or electrical) power conversion factor of 3 to 4. The specific *exergy* consumption of the MSF process using 120°C steam is about 2- to 3-fold higher than that of the RO process, but becomes comparable in magnitude if the steam temperature is lowered to 80°C.

The life of membranes is affected by gradual chemical decomposition or change. For example, cellulose acetate membranes hydrolyze with time. The rate of hydrolysis has a steep minimum at a solution pH of 4.5 to 5.0, and increases drastically with temperature.

Membranes are susceptible to plugging by dirt and to deterioration in their selectivity caused by various species present in the saline water. Careful pretreatment of the feed water is therefore necessary. It typically consists of clarification, filtration, chlorination for destroying organic matter and microorganisms, removal of excess chlorine to prevent membrane oxidation, and dosing with additives to prevent calcium sulfate scaling and foam formation. Periodical chemical or mechanical cleaning is also necessary. Pretreatment and cleaning are significant and increasing fractions of the RO plant capital and operating costs.

Further detail about RO desalination can be found in Sourirajan and Matsuura (1985) and Amjad (1993).

Electrodialysis (ED)

In ED, the saline solution is placed between two membranes, one permeable to cations only and the other to anions only. A direct electrical current is passed across this system by means of two electrodes, cathode and anode, exposed to the solution (Figure 20.6.10). It causes the cations in the saline solution to move toward the cathode, and the anions to the anode. As shown in Figure 20.6.10, the anions can leave the compartment in their travel to the anode because the membrane separating them from the anode is permeable to them. Cations would similarly leave the compartment toward the cathode. The exit of these ions from the compartment reduces the salt concentration in it, and increases the salt concentration in the adjacent compartments. Tens to hundreds of such compartments are stacked together in practical ED plants, leading to the creation of alternating compartments of fresh and salt-concentrated water. ED is a continuous-flow process, where saline feed is continuously fed into all compartments and the product water and concentrated brine flow out of alternate compartments. The flow along the membranes also improves the mass transport there, and the separators between the membranes are constructed to provide good flow distribution and mixing on the membrane surfaces. Membrane sizes are roughly 0.5 × 1 m, spaced about 1 mm apart. Many types of polymers are used to manufacture these ion-exchange selective membranes, which are often reinforced by strong fabrics made from other polymers or glass fibers.

Careful and thorough feed water pretreatment similar to that described in the section on RO is required. Pretreatment needs and operational problems of scaling are diminished in the electrodialysis reversal (EDR) process, in which the electric current flow direction is periodically reversed (say, three to four times per hour), with simultaneous switching of the water flow connections. This also reverses the salt concentration buildup at the membrane and electrode surfaces, and prevents concentrations that cause the precipitation of salts and scale deposition.

The voltage used for ED is about 1 V per membrane pair, and the current flux is of the order of 100 A/m² of membrane surface. The total power requirement increases with the feed water salt concentration, amounting to about 10 MW/m³ product water per 1000 ppm reduction in salinity. About half this power is required for separation and half for pumping. Many plant flow arrangements exist, and their description can be found, along with other details about the process, in Shaffer and Mintz (1980) and Heitman (1991).

Defining Terms

Boiling point elevation: The number of degrees by which the boiling point temperature of a solution is higher than that of the pure solute at the same pressure.

Flash evaporation: An evaporation process that occurs when a liquid with a free surface is exposed to its vapor, where the vapor is below the saturation pressure corresponding to the temperature of the liquid.

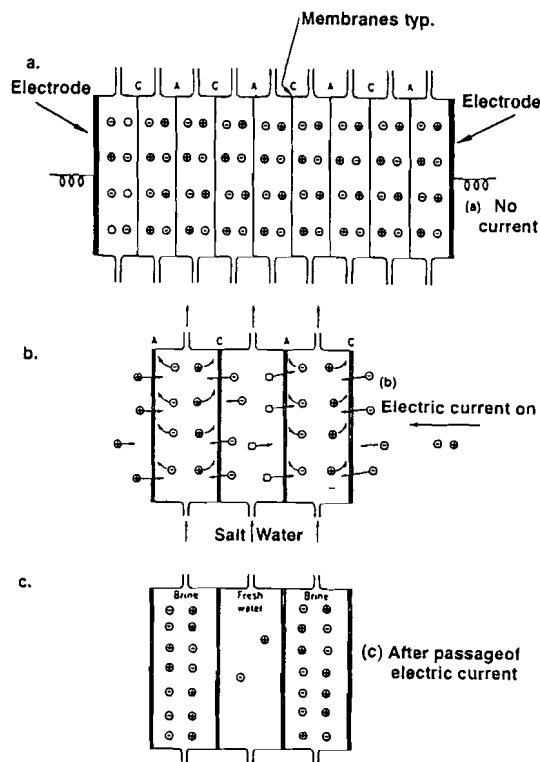


FIGURE 20.6.10 The ED process. C and A are cation- and anion-permeable membranes, respectively. Application of electric current causes ion transport in a way that salt is depleted in alternate compartments, and enriched in the remaining ones.

The process is typically vigorous, accompanied by rapid growth of bubbles and associated turbulence in the liquid.

hydrolysis: Decomposition in which a compound is split into other compounds by taking up the elements of water.

osmosis: The diffusion process of a component of a solution (or mixture) across a semipermeable membrane, driven by the concentration difference (or gradient) of that component across the membrane.

osmotic pressure: The minimal pressure that has to be applied to the solution (mixture) on the lower concentration side of a membrane permeable to one solution component, for stopping the osmosis of that component through the membrane.

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Further Information

The major texts on water desalination written since the 1980s are Spiegler and Laird (1980), Khan, (1986) (contains many practical design aspects), Lior (1986) (on the measurements and control aspects), Heitman (1990) (on pretreatment and chemistry aspects), and Spiegler and El-Sayed (1994) (an overview primer). Extensive data sources are provided in George et al. (1975) and M. W. Kellog (1975).

The two major professional journals in this field are *Desalination*, *The International Journal on the Science and Technology of Desalting and Water Purification* and *Membrane Science*, which often addresses membrane-based desalination processes, both published by Elsevier, Amsterdam.

The major professional society in the field is the International Desalination Association (IDA) headquartered at P.O. Box 387, Topsfield, MA 01983. IDA regularly organizes international conferences, promotes water desalination and reuse technology, and is now publishing a trade magazine *The International Desalination & Water Reuse Quarterly*.

The *Desalination Directory* by M. Balaban Desalination Publications, Mario Negri Sud Research Institute, 66030 Santa Maria Imbaro (Ch), Italy, lists more than 5000 individuals and 2000 companies and institutions in the world of desalination and water reuse.

Two useful (though by now somewhat dated) books on desalination are by Howe, E. D. 1974. *Fundamentals of Water Desalination*, Marcel Dekker, New York, and by Porteous, A. 1975. *Saline Water Distillation Processes*, Longman, London.

Much information on oceans and seawater properties is available in the book by Riley, J. P. and Skinner, Eds. 1975. *Chemical Oceanography*, Academic Press, New York.

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