

CHAPTER 1

Review of Thermal- and Membrane-based Water Desalination Technologies and Integration with Alternative Energy Sources

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1.1. Introduction

Water is the most precious and important resource for human life. The current water scarcity is one of the most serious global challenges. Many countries or regions are augmenting their water supply by desalination to meet the increased water requirement from the increased population, industrial expansion, tourism and agriculture. Water desalination, which is considered as one of the main sources of producing clean water, refers to the process of removing the salts and minerals from either seawater or brackish water to obtain pure water.^{1,2} Especially, some large-scale seawater desalination plants have been built in water stressed countries to augment available water resources. Therefore, there are substantial research interests in finding effective technologies for pure water production. Nowadays, desalination plants operate in more than 120 countries in the world. Figure 1.1 shows the global desalination capacities (m^3/d) and the source water types.³

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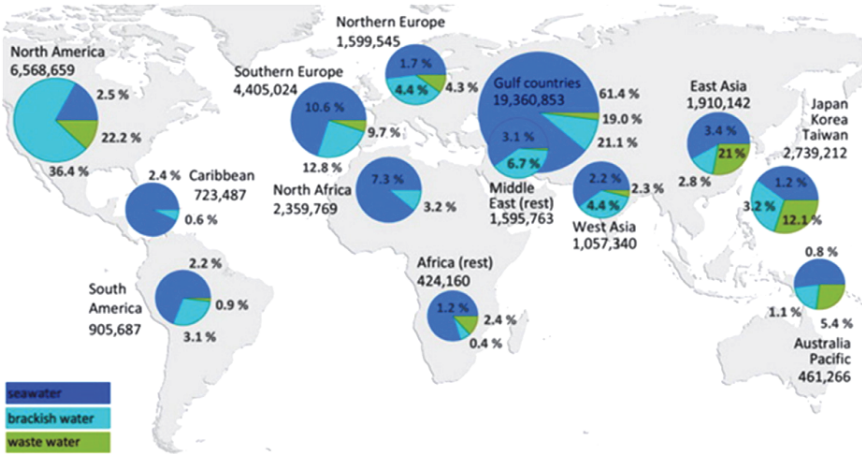


Fig. 1.1. The global desalination capacities (m³/d) and source water types.³

With the development of the desalination technologies, they can be classified into non-membrane based technologies (thermal treatment for water desalination) mostly based on thermal evaporation, and membrane based technologies in which the driving force can be pressure, an electrical potential, a concentration difference or a temperature difference, leading to pressure-driven membranes, electro-driven membranes, concentration-driven membranes and temperature-driven membranes, as shown in Fig. 1.2.⁴

Thermal treatment for water desalination utilizing phase change processes, such as evaporation, precipitation, crystallization, salting out, freezing, solvent extraction and ion-exchange, have been used to produce fresh water. These processes, however, are more energy intensive, and have high capital and operational costs due to their inherent reliance on energy.⁵

Membrane technology for desalination has rapidly developed in recent years due to its separation performance, eco-friendliness due to the lack of production of a secondary pollutant, and its high energy efficiency.^{6,7} With different driving forces, membranes can be classified into pressure-driven membranes (microfiltration, ultrafiltration, nanofiltration and reverse osmosis), electro-driven membranes (electrodialysis and fuel cells), concentration-driven

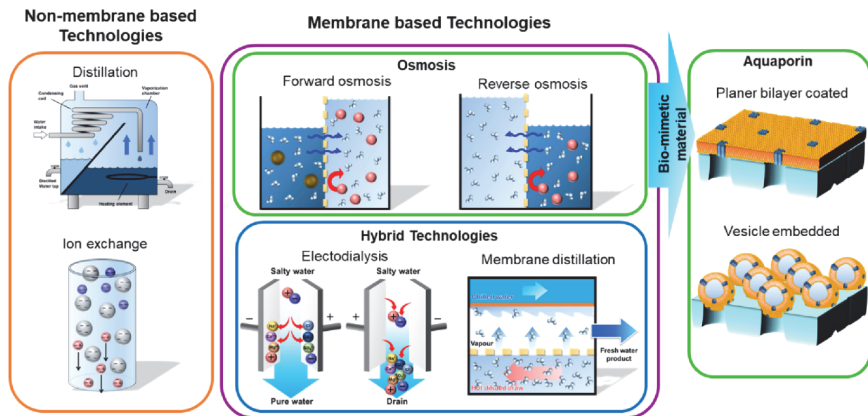


Fig. 1.2. Different desalination technologies.⁴

membranes (dialysis, pervaporation and forward) and temperature-driven membranes (membrane distillation).

In this chapter, thermal methods for water desalination, including evaporation, precipitation, crystallization, salting out, freezing, solvent extraction and ion exchange are summarized. Besides, advanced membrane technologies in water desalination are discussed, with emphasis on nanofiltration and reverse osmosis, electrodialysis and membrane capacitive deionization, forward osmosis and membrane distillation.

1.2. Water Resources

Water is a critical resource of all life. Fresh water is necessary for the economic development of every country of the world, and it is consumed by all economic sectors such as agriculture, industrial, commercial and dwellings.⁸ However, clean water is a scarce and stressed resource since only 2.5% of all the water present on Earth is suitable for direct human use and consumption.⁹ Presently, more than one third of the global population lives in water-stressed countries and it will reach to two thirds in 2025.^{10,11} In addition, in 2030, the latest statistical forecasts have revealed that about half of the Earth's population may face a water stressed condition.¹² These challenges come from the exponentially growing population, continuing industrialization, expanding agricultural activities, water

pollution, poor water management, and climate change. Up to now, many measures to alleviate the stress on water supply should be implemented, including water conservation, repair of infrastructure and improved catchment and distribution systems.¹³ However, these methods still cannot increase the pressure on water availability.

Therefore, desalination of seawater, water from salty lakes, brines or other brackish water is of interest since these sources provide a seemingly unlimited and steady supply of high-quality water. The advances in water desalination technologies are developing fast in recent years. Currently, the water source for desalination are split with about 58.9% from seawater and 21.2% from brackish groundwater sources, and the remaining percentage from surface water and saline wastewater.¹⁴ Numerous large-scale seawater desalination plants have been built in water-stressed countries to augment available water resources. The notable examples are the large-scale membrane separation technologies, such as seawater reverse osmosis (SWRO) desalination plants constructed in Spain and Israel, Qatar and Kuwait rely 100% on desalinated water for domestic and industrial supplies.⁹ The conceptual drawing of seawater reverse osmosis desalination plants is shown in Fig. 1.3.¹⁵ According to

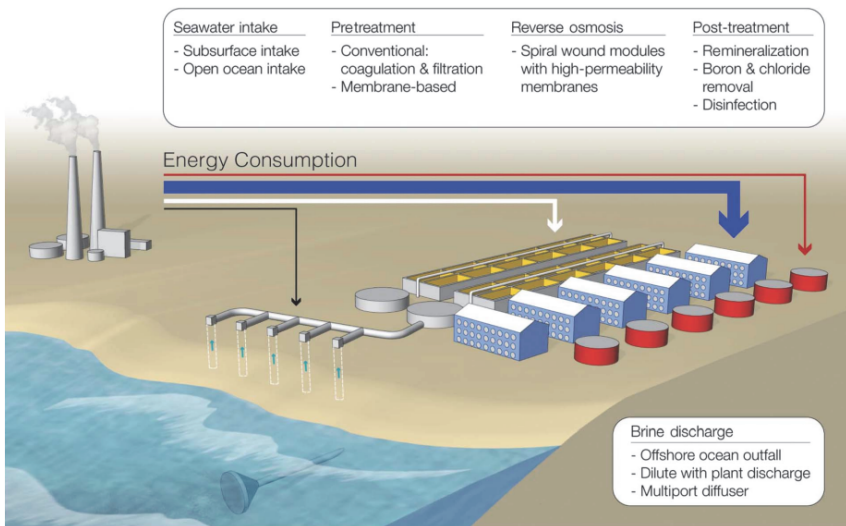


Fig. 1.3. Conceptual drawing of a seawater reverse osmosis desalination plants.¹⁵

the data, the global water production by desalination is over 38 billion m³/year in 2016, and construction of new desalination plants is expected to increase in the near future.¹⁵ According to the literature, a variety of desalination technologies on the basis of thermal distillation, membrane separation, freezing, electrodialysis, etc. has been developed over the years.

1.3. Thermal Treatment for Water Desalination

The thermal treatment for water desalination mainly includes evaporation and freezing.

1.3.1. Evaporation

The evaporation process for water desalination includes multi-stage flash (MSF) distillation, multiple-effect distillation (MED) and vapor compression distillation (VCD).

1.3.1.1. Multi-stage flash distillation

The MSF concept allied with parallel development in technology coincided with an increasing demand for water in arid regions.⁹ The common evaporation method in desalination usually in an MSF distillation process, which is based on the principle of flash evaporation. Different from the approach of raising the temperature, the MSF desalination process is evaporated by reducing the pressure. As shown in Fig. 1.4, the economies of this process are achieved by regenerative heating where the seawater flashing in each flash chamber or stage gives up some of its heat to the seawater going through the flashing process. The heat of condensation released by the condensing water vapor at each stage gradually raises the temperature of the incoming seawater. The MSF plant consists of heat input, heat recovery, and heat rejection sections. These MSF plants usually operate at top brine temperatures of 90–120°C. When the operating temperature is higher than 120°C, the efficiency may be increased, but so is the potential for scale formation and accelerated corrosion of metal surfaces.

In this process (Fig. 1.4), the pressure should remain below the corresponding saturation temperature of the heated inflowing

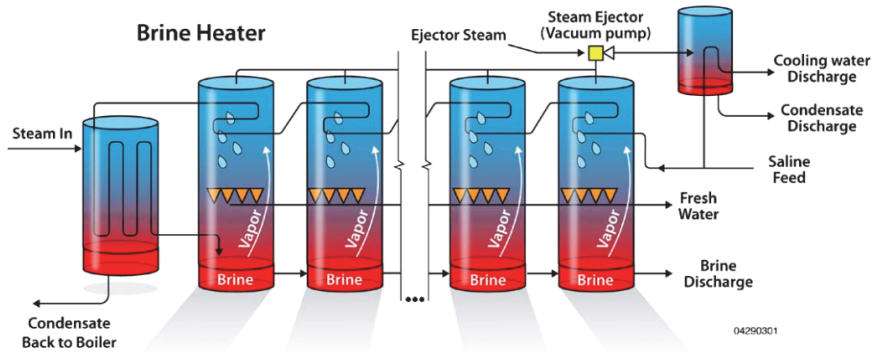


Fig. 1.4. Diagram of a multi-stage flash distillation unit through evaporation.¹⁶

seawater in each stage.¹⁶ The introduction of the salt solutions into the flash chamber causes them to boil rapidly and vigorously. Baffles and orifices installed between stages make the brine's pressure reduce to that of the equilibrium vapor pressure required for boiling at the brine's temperature. Boiling continues until the seawater temperature reaches the boiling point at the stage. The unflushed brine passes from one stage to the next lower pressure stage for further flashing. Thus, the salt solution can be evaporated repeatedly without adding more heat. In this way, each stage of the evaporator is provided with demisters to minimize carryover of brine droplets into the distillate. The flashed water vapor is finally cooled and condensed by colder seawater flowing in tubes of the condenser to produce distillate. Therefore, the fresh water is obtained. Currently, the desalinated water produced by the MSF process in industry contains typically 2–10 ppm dissolved solids.

1.3.1.2. *Multiple-effect distillation*

Multiple-effect distillation (MED) is an important large-scale thermal process offering significant potential for water cost reduction.⁹ The MED process takes place in a series of effects, which are a kind of evaporators, and uses the principle of reducing the ambient pressure in the various effects. This process permits the salt solution to undergo multiple boiling without supplying additional heat after the first effect.

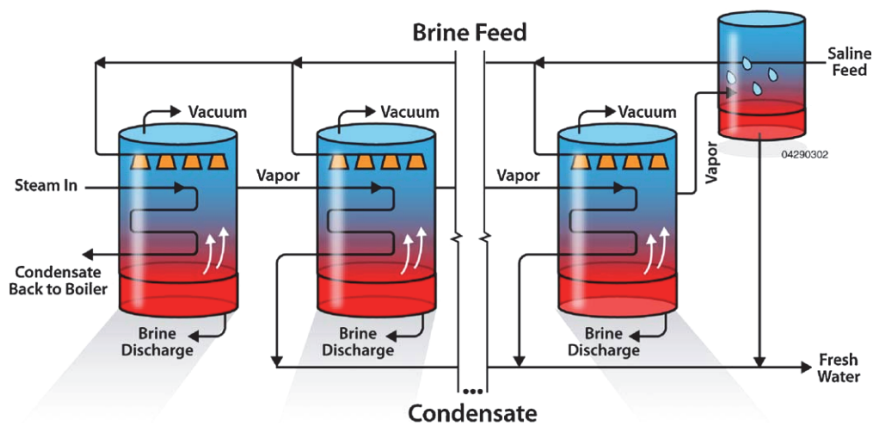


Fig. 1.5. Diagram of a multi-effect desalination unit.¹⁶

In this process (Fig. 1.5), the salt solution enters the first effect and is raised to the boiling point after being preheated in tubes.¹⁶ These tubes are heated by externally supplied steam. The steam is condensed on the opposite side of the tubes. Then, the steam condensate is recycled to the power plant for its boiler feedwater. The MED plant's steam economy is proportional to the number of effects. The total number of effects is limited by the total temperature range available and the minimum allowable temperature difference between each of the effects. In this process, the evaporation and condensation are repeated from effect to effect each at a successively lower pressure and temperature. The energy consumption of the MED plant is significantly lower than that of an MSF plant. The performance ratio of the MED plant is higher than for an MSF plant.

1.3.1.3. Vapor compression distillation

Vapor compression distillation (VCD) includes mechanical vapor compression desalination (Fig. 1.6(a)) and thermal vapor compression desalination as two similar methods (Fig. 1.6(b)), in which the heat for evaporating the seawater comes from the compression of vapor.¹⁶ Through reducing the pressure, the VCD plants take advantage of the principle of reducing the boiling point temperature.

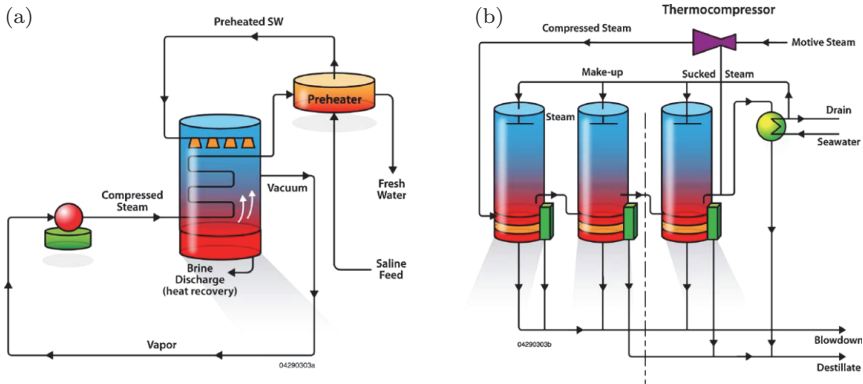


Fig. 1.6. Diagram of a mechanical vapor compression (a) and diagram of a thermal vapor compression (b) for desalination.¹⁶

The mechanical vapor compression desalination process is usually electrically driven. The VCD units are built in a variety of configurations to promote the exchange of heat to evaporate the salt solution. The compressor creates a vacuum in the evaporator and then compresses the vapor taken from the evaporator and condenses it inside a tube bundle. The salt solution is sprayed on the outside of the heated tube bundle where it boils and partially evaporates, producing more vapor.

The thermal vapor compression desalination process with the steam-jet type of VCD unit, a venturi orifice at the steam jet creates and extracts water vapor from the evaporator, and then creates a lower ambient pressure. The extracted water vapor is compressed by the steam jet. VCD units are often used for resorts, industries and drilling sites where fresh water is not readily available.

1.3.2. *Freezing*

In the freezing process, the salts are removed from salty water by the formation of ice crystals, which do not contain any salt.¹⁷ Before water has been frozen, the mixture is usually washed and rinsed to remove the salts in the remaining water or adhering to the ice and then the ice is melted to produce fresh water. The freezing process is made up of cooling of the salt solution feed, partial

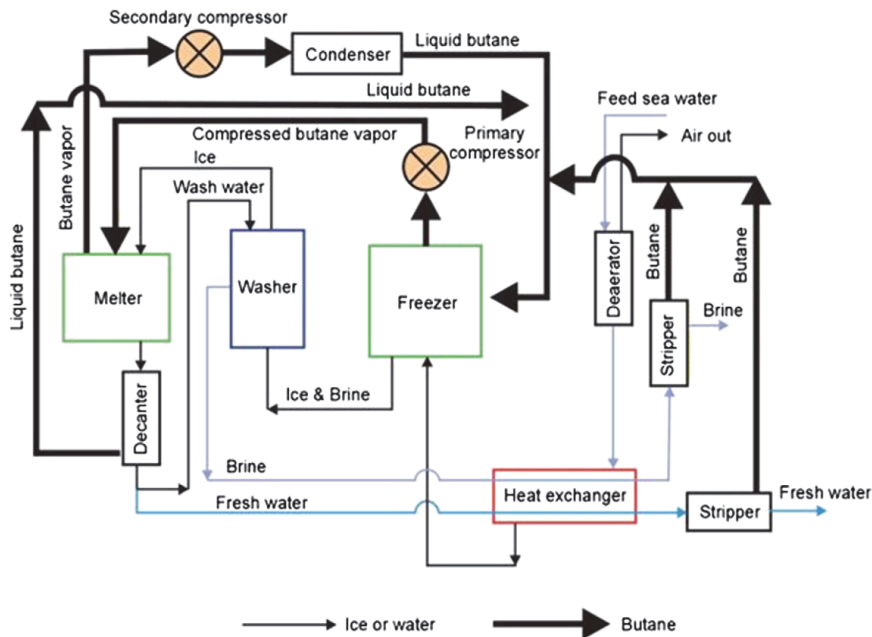


Fig. 1.7. Schematic diagram of a direct contact freezing process for desalination.¹⁹

crystallization of ice, separation of ice from seawater, melting of ice, refrigeration and heat rejection.¹⁸ Usually, it contains the triple point freezing process, secondary refrigerant freezing process, eutectic freezing process, hydrate freezing process and direct contact freezing process (Fig. 1.7).¹⁹ The advantages of freezing desalination are in the lower theoretical energy requirement, minimal potential corrosion, and little scaling or precipitation. The disadvantage of freezing involves handling ice and water mixtures, which are mechanically complicated to move and process.

1.4. Pressure-Driven Membranes Process in Water Desalination

Reverse osmosis (RO) and nanofiltration (NF) are the two pressure-driven membrane processes whereby a semi-permeable membrane rejects dissolved constituents present in the feed water.²⁰ They

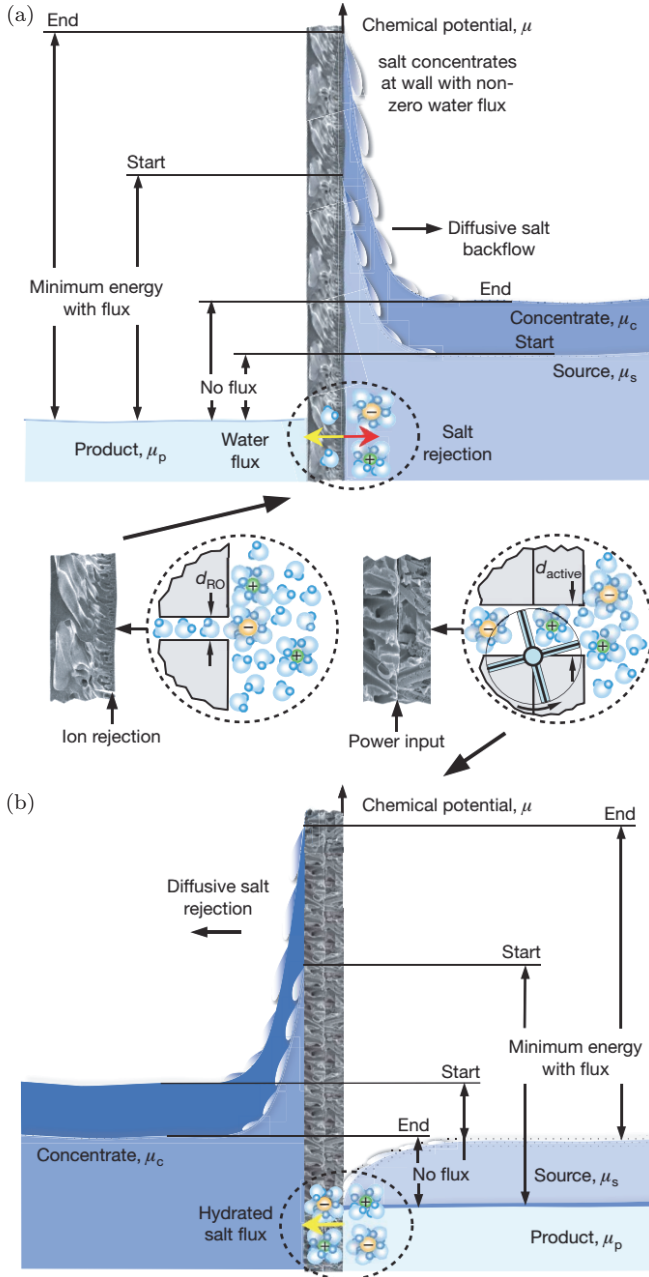
are gaining worldwide acceptance in both water treatment and desalination applications. One of the most important indices is rejection, which is due to membrane size exclusion, charge exclusion and physical/chemical interactions between solute, solvent and membranes. The process efficiency depends on operational parameters, membrane performance and feed water properties.²¹

1.4.1. *Reverse osmosis*

Osmosis, in simple terms, can be defined as a natural process in which water molecules spontaneously move from a solution of low osmotic pressure to a solution of high osmotic pressure across a semipermeable membrane.^{22,23} The membrane, being semipermeable, rejects the solutes and only allows water molecules to pass through and until a state of osmotic equilibrium is reached where the chemical potentials across the membrane become balance.²⁴ In case the applied pressure difference is greater in magnitude than the osmotic pressure difference across the membrane, water molecules are forced to flow in a direction opposite to that of the natural osmosis phenomenon, as shown in Figs. 1.8(a) and 1.8(b).¹³

Presently, seawater or salt lake water RO dominate the global desalination market based on installed capacity. The major components of RO are four major units, the pretreatment, pumping, membrane assembly and post treatment units.

In the RO process, pretreatment is needed to eliminate undesirable constituents in the seawater, which would otherwise cause membrane fouling. Therefore, raw feed flows into the intake structure through trash racks and traveling screens to remove debris and finally obtain the cleaned salt solution after a filter process. As shown in Fig. 1.9, the filtered feed provides a protection to the high-pressure pumps and the RO section of the plant. The high-pressure pump raises the pressure of the pretreated feed water to the pressure appropriate for the RO membrane.¹⁵ The osmotic pressure is overcome by applying an external pressure higher than the osmotic pressure on the seawater and then the water flows in the reverse direction to the natural flow across the RO membrane, leaving the dissolved salts behind with an increase in salt concentration. In this



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Fig. 1.8. Concentration gradients in RO (a) and active (b) desalination membranes.¹³

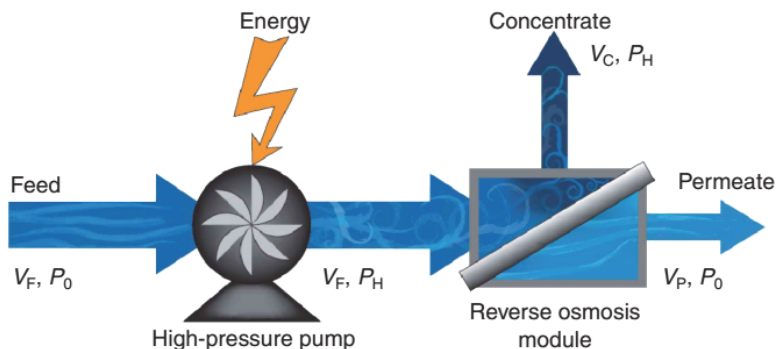


Fig. 1.9. A schematic of flows and pressures in a reverse osmosis desalination system.¹⁵

process, no heating or phase separation change is necessary. The major energy required in the RO process is for pressurizing the salt solution feed. Major design considerations of RO plants are the quantity of flux, conversion or recovery ratio, permeate salinity, membrane life, power consumption, and feedwater temperature.

The RO membrane is the core part of this technology. In a continuous RO process, recovery or conversion of the RO process is defined as the volume fraction of feed water that is recovered as permeate or product water. The percentage recovery (r) can be calculated as follows

$$r = \frac{Q_P}{Q_F} \times 100\%$$

where Q_P and Q_F are the flow rates of the permeate and feed streams, respectively. The salt rejection (SR) is defined as the percentage of a particular incoming solute that is rejected by the RO membrane. The apparent SR is given as

$$SR = \left(1 - \frac{c_P}{c_F} \right) \times 100\%$$

where, c_P and c_F represent permeate and feed solute concentration (mg/L), respectively. RO membranes can easily remove 95 to 99% of dissolved salts, solid particles, biological contaminants and other organic contaminants from the feed. The rejection efficiency relies on

two factors, the charge of the membrane surface and the pore size of the membrane structure. Typically, the water flux is proportional to the net pressure driving force across the membrane. The permeate or water flux (J_w) is the volumetric flow rate of permeate per unit surface area of the RO membrane.

As RO works against osmosis, a variety of polymer-based membranes that can withstand this high pressure are employed, and they can be broadly categorized. According to the data, non-cellulose polyamide is the most commonly used material for RO membranes because of its high-water permeability and salt rejection. These RO membranes consist of a porous support with an active thin polyamide layer, which is responsible for salt rejection and water permeability. Additionally, these membranes offer a wide range of operational pH and temperatures but are highly sensitive to oxidizing agents. The major drawback of these polyamide membranes is fouling, which is mainly related to the hydrophobicity of the membrane surface.

There are four different types of RO membranes modules: plate and frame, tubular, spiral wound and hollow fiber. Among these, the plate and frame modules are the earliest RO membrane modules.²⁵ As shown in Fig. 1.10(a), a flat sheet RO membrane is attached to the two sides of a rigid plate. A number of plates are used that are stacked within a pressurized support framework. These plates contain grooved channels that provide a path for the permeate flow. As the feed solution enters the module from one end, water molecules permeate the membrane and are collected as permeate solution in a central permeate collection manifold and the concentrate salt solution leaves the module from the other end. Tubular modules, as shown in Fig. 1.10(b), are relatively simple in construction, and consist of a porous tube with an inserted or surface coated RO membrane. The tubes are made of ceramic, carbon, paper, plastic, or fiberglass. As high-pressurized feed water enters the tube from one end, water molecules permeate radially through the membrane to produce the product water. The concentrate salt solution leaves from the other end of the tube. Multiple tubes can be arranged in series or parallel to increase the system capacity. The hollow fiber module is composed of many small-diameter fibers contained within

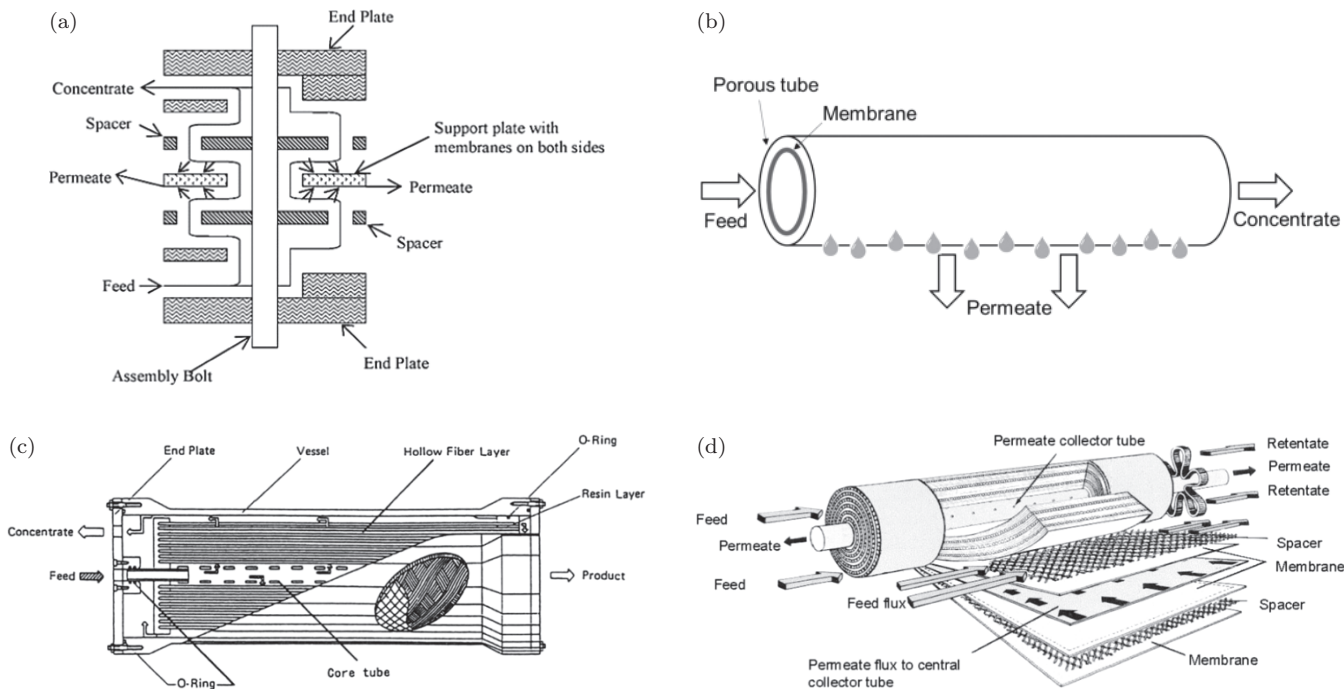


Fig. 1.10. Plate and frame RO membrane module (a), tubular RO membrane module (b), hollow fiber RO membrane module (c) and spiral wound RO membrane module (d).²⁵

a pressure vessel. As shown in Fig. 1.10(c), the module consists of an epoxy tube sheet where the fibers ends are potted in epoxy while keeping them open for permeate flow, and the fiber ends are sealed in epoxy to form an epoxy nub, which prevents bypassing of the feed to the concentrate outlet. In this structure of a hollow, as pressurized feed water enters the module through the core tube, water molecules permeate radially into the fibers and exit pass the open fiber ends in the epoxy tube sheet while the concentrate leaves the module at the same end as the feed inlet. Figure 1.10(d) shows the spiral wound modules, which currently are the most common type of module applied for RO desalination. In this module, two membrane sheets are placed together with a permeate spacer in between to form a leaf. The membrane sheets are glued from three sides with the fourth side left open and connected to a central perforated permeate collector tube. In this module, the feed solution is introduced from one end of the module and travels axially along the length of the module. Water molecules are forced cross the membrane and are collected as permeate through the perforated permeate collector tube. The concentrate leaves the module at the end opposite to the feed.

1.4.2. *Nanofiltration*

Nanofiltration (NF) as an effective pressure-driven membrane process has a pore size and cut off ability between RO and ultrafiltration (UF).^{26,27} Compare to RO, the NF process operates not only at lower operation pressures, higher water fluxes, and lower investment costs, but also with comparably high rejection rates for scale formation bivalent ions.²⁸ NF is dependent on the micro-hydrodynamic and interfacial events occurring at the membrane surface and within the membrane nanopores.²⁹ As the key compartment of NF technology, typically, the formation of NF membranes involves phase inversion followed by interfacial polymerization to produce thin-film composite (TFC) membranes, as shown in Fig. 1.11.^{27,30,31} Current progress in preparation methods includes the incorporation of additives such as nanoparticles

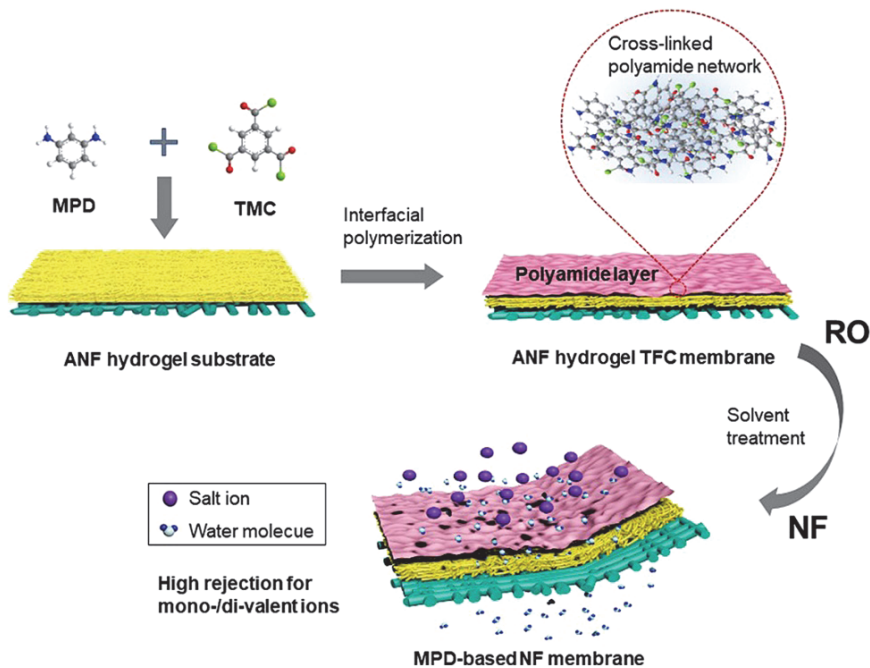


Fig. 1.11. Polyamide/Kevlar aramid nanofiber nanofiltration membranes for water desalination.²⁷

in the thin film layer to enhance the separation properties. As shown in Fig. 1.12, the recent development of NF membrane technology has been in terms of creating better filtration technologies in wastewater treatment, food industry, solvent nanofiltration, desalination etc.³²

The rejection obtained with NF membranes may be attributed to a combination of steric (membrane pore size sieving), Donnan (describe the equilibria and membrane potential interactions between a charged species and the interface of the charged membrane), dielectric and transport effects.³³ In application, NF is often combined with other membrane-based desalination processes, including dual stage NF desalination, integrated NF and RO desalination processes, integrated NF and forward osmosis (FO) desalination processes, and integrated NF and electrodialysis (ED) desalination processes.

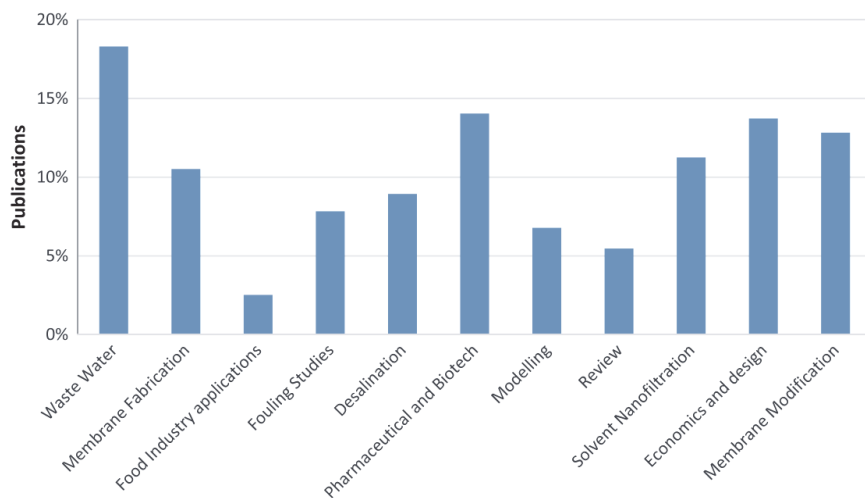


Fig. 1.12. The research topics of nanofiltration membrane process covered in the articles reviewed (2007–2017).³²

1.5. Concentration-Driven Membranes Process in Water Desalination

Forward osmosis (FO) is an osmotically driven membrane separation process, which depends on the concentration gradient between the two sides of the membrane; water moves from a feed solution across a semipermeable membrane to a draw solution.³⁴ The driving force for mass transport is coming from the difference in osmotic pressure between the feed solution and a draw solution, which is caused by the concentration of solutions. Water diffuses from the feed solution of higher chemical potential (lower concentration) to a draw solution of lower chemical potential (higher concentration). With different concentration, an osmotic pressure difference builds up. This is used for water recovery enhancement in desalination of salt solutions, as shown in Fig. 1.13. As water diffuses through the membrane, the feed solution becomes concentrated and the draw solution is diluted; and thus, the draw solution must be re-concentrated in order to maintain the osmotic pressure driving force.³⁵ This process was considered by some scientists for the industrial purification of water due to the low energy composition. Without the energy driven advantage, FO draws

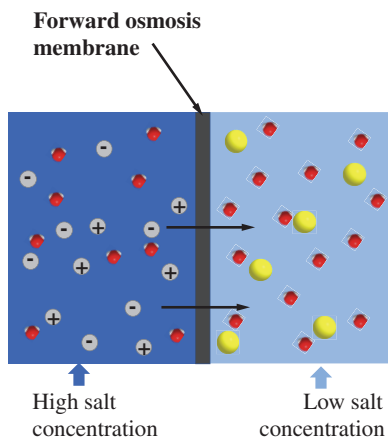


Fig. 1.13. Scheme of the osmosis desalination system.

a large portion of water from a feed, making it suitable for water contaminated with particulate and biological agents, especially for desalination.

However, the implementation of FO in water desalination has been limited by a few technical challenges, not the least of which is the draw solute (Fig. 1.13). In an FO system, when using conventional draw solutes, either the draw solute is incorporated into the final product or remove it through other separate processes. A standing challenge to the success of industrially relevant FO is the development of a next generation draw solute that can provide a significant osmotic pressure but be separated from water by means other than RO.³⁶

The performance of the FO process was evaluated using a bench-scale membrane test unit coupled with a pilot-scale RO system. In this system, the pilot-scale RO system supplied the FO system with a constant-concentration draw solution, as shown in Fig. 1.14. The draw solution was recirculated on the support side of the FO membrane and its conductivity was measured by using a conductivity meter.³⁷ Therefore, the salt rejection (SR) is defined as the percentage of a particular incoming solute that is rejected by the

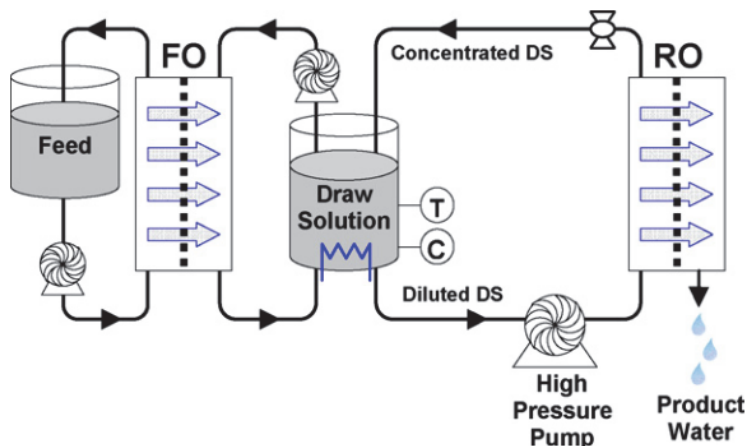


Fig. 1.14. Schematic drawing of the combined bench-scale FO and pilot-scale RO systems.³⁷

FO membrane, which is given as

$$SR = \left(1 - \frac{c_P}{c_F}\right) \times 100\%$$

where, c_P and c_F represent permeate and feed solute concentration, respectively.

1.6. Electro-Driven Membranes Process in Water Desalination

Electrodialysis (ED) and membrane capacitive deionization (MCDI) are the two electro-driven membrane separation technologies, which are widely used in water desalination. Over the past decade, the development of electro-driven membranes processes has attracted increasing research attention in terms of materials, preparation and application, because of their potential in water treatment.^{38–40} Different from pressure-driven membranes and concentration-driven membranes, the electro-driven membranes are composed of polymeric materials bearing covalently bound ionic fixed charges.^{41,42} Only the ions with opposite charges to the surface charge of the membranes are transported through the membrane; while ions with

the same charge are electrostatically repelled and retained in the feed compartment.

1.6.1. *Electrodialysis*

ED has been widely used for separation of cation/anion by different ion exchange membranes (IEMs) and has been applied on a large industrial scale for over 60 years. In the ED process, ions from the diluted compartment flow through IEMs to the concentrated compartment under the electric field. ED is used to produce pure water from brackish water, industrial waste and seawater.⁴³ The ED technology has four main parts, which is IEMs, electrode chamber, diluted chamber and concentrated chamber, as shown in Fig. 1.15. The key element of the ED process is the IEM, including anion exchange membranes (AEMs), cation exchange membranes (CEMs) and bipolar membranes (BMs). Cations/anions are selectively transported from one compartment (the diluted compartment) to another compartment (the concentrated compartment) through electro-driven membranes. Water molecules split into H^+ and OH^- by BMs in this process.

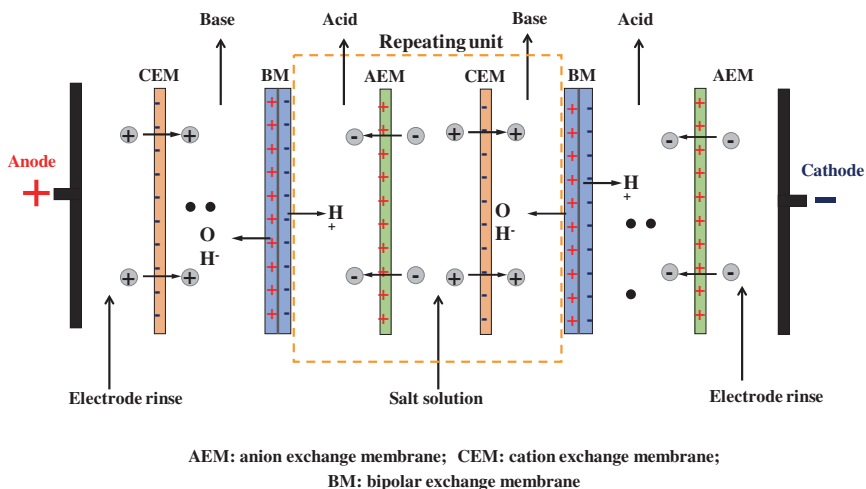


Fig. 1.15. The scheme of electrodedialysis.

Based on the theories of Donnan equilibrium, chemical potential equilibrium and the electric double layer, anions and cations selective separation under the electric field force. The Donnan potential φ_{Don} and is given as

$$\begin{aligned} \varphi_{\text{Don}} &= \varphi^m - \varphi^s = \frac{1}{z_i F} \left(RT \ln \frac{a_i^s}{a_i^m} + V_{m_i} (p^s - p^m) \right) \\ &= \frac{1}{z_i F} \left(RT \ln \frac{a_i^s}{a_i^m} + V_{m_i} (\Delta\pi) \right) \end{aligned}$$

where F is the Faraday constant; z_i is the charge number of the ions i in the solution; R is the gas constant and T is the temperature; V_{m_i} is the partial molar volume of component I ; $\Delta\pi$ is the osmotic pressure difference between the membrane and the adjacent solution, which is also referred to as the swelling pressure of the membrane. The Donnan potential φ_{Don} cannot be measured directly. It can, however, be calculated from the ion activities in the solution and the membrane and by the swelling pressure $\Delta\pi$.

In the ED process, the desalination property is defined by the desalination rate (D),⁴⁴ which is defined as

$$D = \left(1 - \frac{c_t}{c_0} \right) \times 100\%$$

where c_t represents the concentration of the ion in dilute cell at time, t in the time and c_0 is its initial dilute in concentrated cell.

It is also can be illustrated by concentrated rate (C), which is defined as

$$C = \left(\frac{c'_t}{c'_0} - 1 \right) \times 100\%$$

where c'_t represents the concentration of the ion in concentrated cell at time, t in the time and C_0 is its initial concentration in concentrated cell.

The energy consumption (EC) required in an ED process is the sum of the electrical energy to transfer the ionic species through ion selective membranes and the energy required to pump various solutions through the ED stack. It is a measure of the power

consumed in Watthour per liter (Wh/L) for transport of ions and is calculated by

$$EC = \frac{E \int_0^t I dt}{V_D}$$

where E is the potential (V), I is current (A), V_D is the volume of the diluate (m^3), and t is time (s).

Usually, ED uses an assembly of alternatively stacked anion and cation exchange membranes to separate ions or produce pure water, as shown in Fig. 1.16, a series of AEMs and CEMs arranged in an alternating pattern between two electrodes.⁴⁵ In this process, ions from the diluted compartment pass through AEMs/CEMs to the concentrated compartment under the electric field. In an industrial size ED stack, hundreds of cell pairs are arranged between the electrodes. Different constructions of spacers and stacks such as sheet flow or tortuous path flow stack designs are applied.

In this process, the degree of desalination that can be achieved by passing the feed solution through a stack is a function of the solution

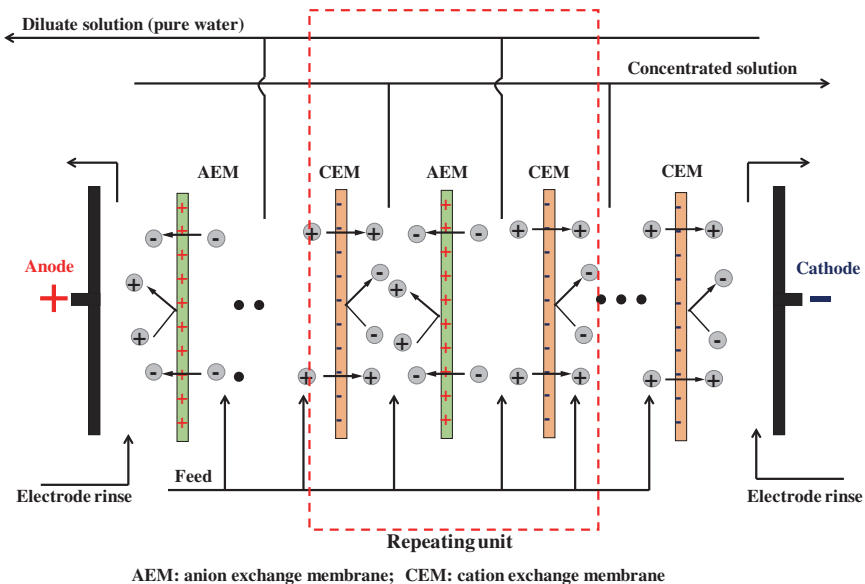


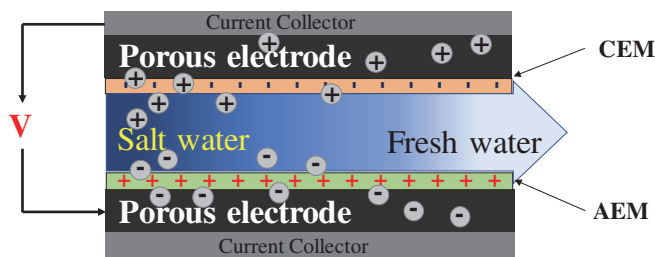
Fig. 1.16. Desalination by electrodesalination.

concentration, the applied current density, and the residence time of the solution in the stack. In the feed and bleed operating mode, both the brine and the product concentration can be determined independently, and very high recovery rates or brine concentrations can be obtained. In conventional ED, several indices should be measured:

- (1) Concentration polarization and limiting current density, which is the electrochemical behavior of electro-driven membranes in ED separation process;
- (2) The total energy required in electrodesalination for the actual desalination process is given by the current passing through the electrodesalination stack multiplied by the total voltage drop encountered between the electrodes.^{46,47}

1.6.2. Membrane capacitive deionization

Membrane capacitive deionization (MCDI) consists of a porous electrode of an inexpensive commercial activated carbon fiber (ACF) and AMEs and CEMs into the cell compartment, as shown in Fig. 1.17. MCDI operation requires electricity, which makes it an electro-driven membranes process. It is an energy-efficient and environment-friendly desalination technology. In the MCDI cell, under a direct current electric field between two porous electrodes arranged in parallel, ions are removed from salt solutions by electrical migration. It is especially advantageous for treatment of low concentration salt solutions (lower than 5 g/L). Recent MCDI research is focused on exploiting high



AEM: anion exchange membrane; CEM: cation exchange membrane

Fig. 1.17. Desalination by capacitive deionization.

performance porous electrode materials, such as carbon nanofibers, mesoporous carbon, graphene and carbide-derived carbon.

Currently, three main strategies are proposed for further development of MCDI electrode materials:

- (1) developing novel electrode materials with high electric chemical performances and lower cost;
- (2) enhancing the commercial electrode materials performance through surface modifications or optimization of the MCDI cell design;
- (3) adding the suitable AEMs and CEMs into the cell compartment to increase the desalination rate, salt removal efficiency and charge efficiency.

Figure 1.18 shows the scheme of MCDI and the desalination process in the lab. The cell is assembled by a retaining plate, titanium

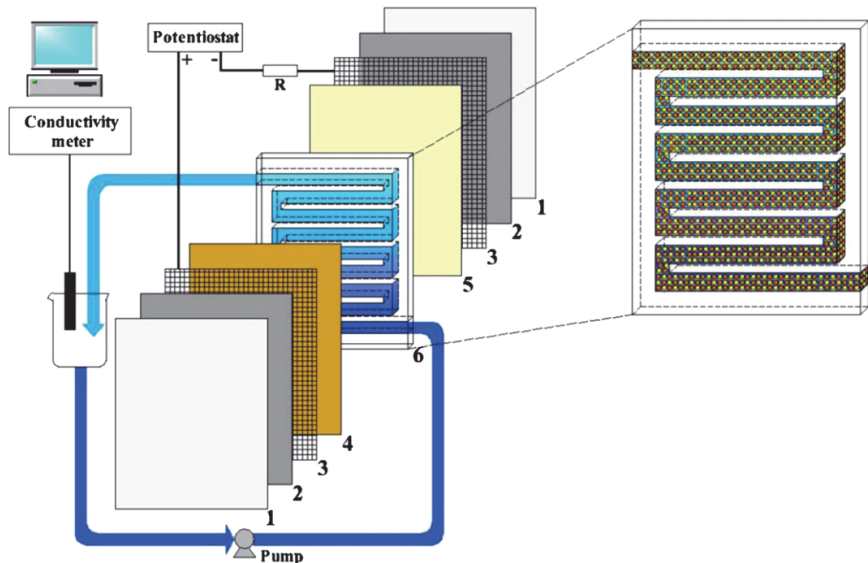


Fig. 1.18. Schematic diagram of a membrane capacitive desalination.⁴⁸ 1. retaining plate; 2. titanium plate; 3. activated carbon fiber electrode; 4. anion exchange membrane; 5. cation-exchange membrane; 6. rubber gasket with an S-shape channel.

plate, activated carbon fiber (ACF) electrode, anion exchange membrane, rubber gasket with an S-shaped channel, cation exchange membrane, ACF electrode, titanium plate and retaining plate. The 2-mm thick rubber gasket serves as the spacer between two ACF electrodes to avoid short circuit and allows the salt solution to flow through its S-shaped channel. In this process, the salt solution is pumped into the tested MCDI cell at a constant flow by using a peristaltic pump and the effluent is continuously recycled.⁴⁸ The electrical conductivity of the salt solution is monitored at the outlet of the MCDI cell using an online conductivity meter.

The desalination performance of MCDI is evaluated by the salt removal efficiency and the desalination rate. The salt removal efficiency is defined as,

$$\eta = \left(1 - \frac{c_e}{c_0}\right) \times 100\%$$

where c_0 and c_e refer to the initial and final concentration of the salt solution, respectively.

The desalination rate is calculated as,

$$v_1 = \frac{c_0 - c_e}{T_1}$$

where T_1 is the duration of the adsorption stage in an adsorption/desorption cycle.

The desorption rate is defined as,

$$v_2 = \frac{c_f - c_e}{T_2}$$

where T_2 is the duration of the desorption stage in an adsorption/desorption cycle, c_f is the salt solution concentration at the end of the desorption stage.

The charge efficiency is calculated as

$$\eta = \frac{(c_0 - c) \times V \times F}{M \times \sum it} \times 100\%$$

where V is the volume of the salt solution (m^3), F is the Faraday constant, which is 96,485 C/mol; M is the molecular weight of the salt; and i is the current (A) at time t (s).

1.7. Temperature-Driven Membranes Process in Water Desalination

Membrane Distillation (MD) is a temperature-driven membrane separation process in which only vapors can pass through a porous hydrophobic membrane, as shown in Fig. 1.19. The separation is achieved due to the vapor pressure differences between the membrane surfaces. As the core part of MD process, the membranes used for membrane distillation must be highly hydrophobic, highly porous and must have low thermal conductivity. Besides, the permeate flux increases with the increase in pore size and reduction in membrane thickness. The operating parameters including feed water temperature, flow rate, thickness of air gap, thickness of membrane, thermal conductivity of membrane, porosity, tortuosity and long-term operations have an effect on the distillate yield.

For these membranes, membrane porosity is given by

$$\varepsilon = 1 - \frac{\rho_m}{\rho_{pol}}$$

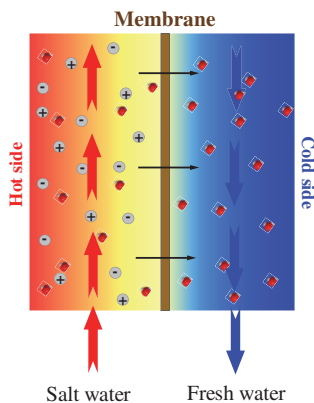


Fig. 1.19. Membrane distillation process for desalination.

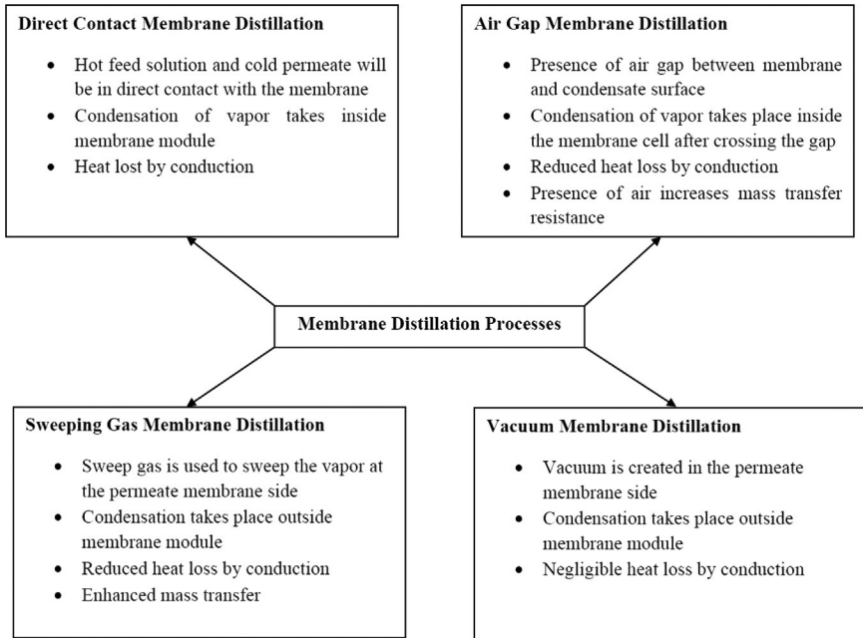


Fig. 1.20. Types of membrane distillation processes.

membrane tortuosity is given by

$$\tau = \frac{(2 - \varepsilon)^2}{\varepsilon}$$

There are four main types of membrane distillation processes, namely air gap membrane distillation, sweeping gas distillation, direct contact membrane distillation and vacuum membrane distillation. The salient features of each membrane distillation process are shown in Fig. 1.20. All these processes, the hot feed solution is in direct contact with the membrane surface.

1.8. New Energy-Drive Process in Water Desalination

1.8.1. Solar energy process in water desalination

Solar energy is a common and most promising source for boosting the evolution of renewable energy technology. In past decades,

solar-to-thermal technologies, such as domestic heating, salt-water desalination and power generation, have been the subject of both academic research and industrialization efforts.⁴⁹ Despite the unmatched resource potential of solar energy, the restricted utilization efficiency presents an enormous challenge.⁵⁰

Solar vapor generation, which can directly transfer heat to facilitate evaporation, is an efficient way of harvesting solar energy for water desalination and obtain fresh water.⁵¹ The use of direct solar energy for desalinating salt-water has been investigated extensively. It is similar to a part of the natural hydrologic cycle in which the salt-water is heated by solar energy to produce water vapor. Then, the water vapor is condensed on a cool surface, and the condensate collected as product water.⁵² A common example of this type of process is the green house solar still, in which the salt water is heated in a basin on the floor and the water vapor condenses to be a fresh water on the sloping glass roof that covers the basin, as shown in Fig. 1.21. Solar-still designs can generally be grouped into four categories, which are the basin still, tilted-wick solar still, multiple-tray tilted still and concentrating mirror still. The basin

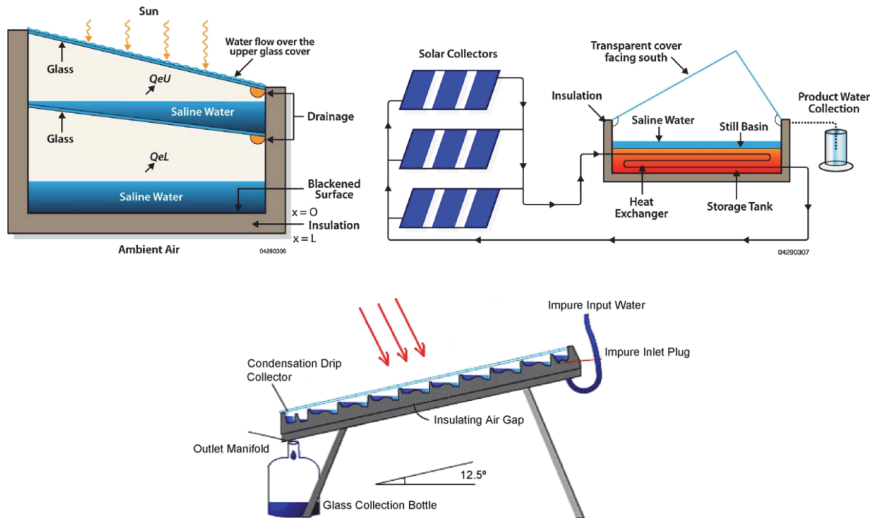


Fig. 1.21. Schematic diagrams of a simple solar still.

still consists of a basin, support structure, transparent glazing, and distillate trough.

Because solar radiation is the only power input for vapor generation, a lot of materials, including ultra-black absorbers, plasmonic nanoparticles and thermal-concentrating ceramics, have been used to enhance the conversion efficiency. In addition, variations of this type of solar still have been made in an effort to increase efficiency.⁵³ However, the requirement of a large solar collection area, high capital cost, vulnerability to weather-related damage and the inefficient utilization of converted heat imposes challenges. Of the solar energy process in water desalination, the three major heat consumption processes, which are water heating, parasitic thermal loss and water vaporization, only water vaporization is effective. Therefore, adequate thermal management in the solar vapor generation system is essential. The heat localization strategy, which restricts heat into a small amount of water in the evaporating surface, may substantially improve the efficiency of solar energy utilization.

1.8.2. Nuclear energy in water desalination

Compare to fossil fuels, nuclear power in particular received a considerable attention with its potential of less expensive nuclear fuel costs and highly efficient energy. Currently, energy production from all of the operating nuclear power plants utilizes the process of nuclear fission. During the nuclear fission, a huge amount of energy is released due to the split of heavy atomic nuclei in order to form lighter atomic nuclei. The nuclear energy offers a higher energy density compared to other conventional and renewable energy sources. With the continuous depletion of fossil fuels, continuous population growth, and the increase demand for fresh water, developing countries are currently interested in the development of nuclear reactors. According the International Atomic Energy Agency (IAEA) data, the nuclear power generation is expected to increase in the coming decades along with the applied policies towards the reduction in carbon dioxide emissions.

Nuclear energy in water desalination appears to be a feasible and a promising technical option to power desalination plants at

reasonable costs. It is the process of producing fresh water by using an on-site nuclear reactor from salt-water. Plant capacity and water quality are among the several factors that can significantly affect the energy demand in any desalination process. In 1970s, in Kazakhstan and Japan, the nuclear desalination plants were first established. According to the type of coolant used, generally, there are two types of nuclear reactors that are used in desalination:

- (1) light water reactors (LWR);
- (2) the heavy water reactors (HWR).

For LWR category, it is also including boiling water reactors and pressurized water reactors; For HWR category, it is including pressurized heavy water reactors. There are other types such as the Liquid Metal Fast Breeder Reactor and high temperature gas cooled reactor. In general, the water-cooled reactors are preferred because of the well-established technology. In the literature, Pressurized Water Reactor, Pressurized Heavy Water Reactor and Liquid Metal Fast Breeder Reactor are the most common nuclear reactors coupled with desalination processes.

Figure 1.22 shows the nuclear energy process in water desalination, including a multi-effect distillation (MED) and an RO. The purpose is to generate electricity as well as utilizing the waste heat to produce steam that will be fed into the MED unit. To design a nuclear energy process in water desalination, the following steps should be performed:

- (1) proper modeling for the reactor-desalination systems;
- (2) careful evaluation for the nuclear plant safety;
- (3) technical outcomes from the desalination process itself.⁵⁴

Up to now, ten main projects around the world have launched to perform study and optimization for nuclear energy utilization in water desalination: INVAP in Argentina, CANDESAL in Canada, INET in China, NPPA in Egypt, BARC in India, KAERI in the republic of Korea, CNESTEN in Morocco, OPPE, OKBM, JSC in Malaya, Energetica in Russia and CNSTN in Tunisia. In addition, more and more countries are currently considering the nuclear energy process in water desalination. Whether this is a good option, taking

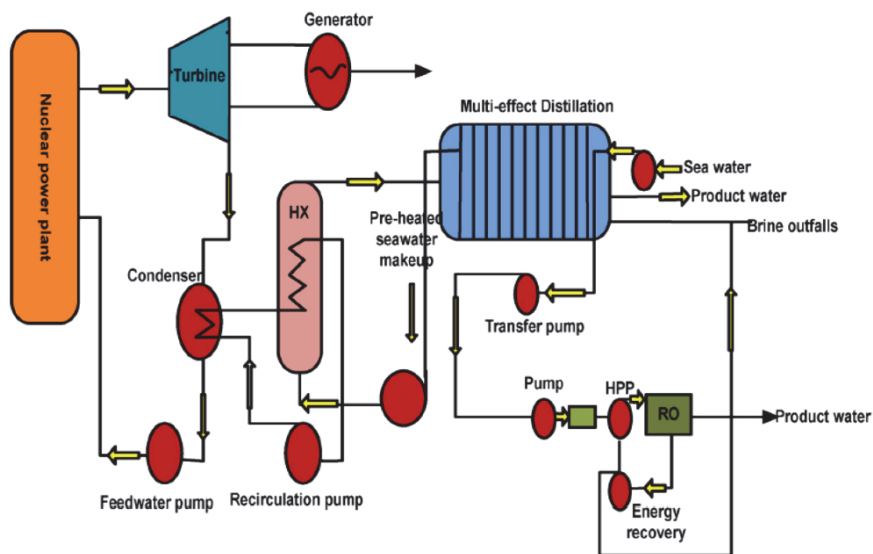


Fig. 1.22. A schematic diagram for a nuclear desalination process. HX: Heat Exchanger, and HPP: High Pressure Pump.⁵⁴

the full environmental picture and the limited availability of uranium into account, remains however questionable.

1.8.3. Wind energy in water desalination

Wind turbines can be used to supply electricity or mechanical power in water desalination. Few applications have been implemented using wind energy to drive a mechanical vapor compression unit. Usually, the possible combination with wind energy process in water desalination are the mechanical compressor (MVC) and RO by the shaft, and ED, MVC and RO by the electricity. An example of the first world pilot plant was installed in 1991 at Borkum, an island in Germany, where a wind turbine with a nominal power of 45 kW was coupled to a 48 m³/day MVC evaporator.¹⁶

1.9. Conclusions and Outlook

Recent years, numerous large-scale salt lakes or seawater desalination plants have been built in water-stressed countries and regions to augment available water resources, and construction of new

desalination plants is expected to increase in the coming decades. Especially, the surging population growth, urban development, and industrialization will increase worldwide demand for fresh water, requiring new sources of water. Desalination offers the potential for an abundant and steady source of fresh water purified from the vast oceans or salt lakes. Many advanced technologies in desalination have been developed for the treatment of fresh water. For water-stressed countries and regions that already implement all other measures for freshwater generation, these advanced technologies may serve as the only viable means to provide the water supply necessary to sustain agriculture, support population and promote economic development.

Among these advances in water desalination technologies, membrane technology, especially the RO desalination process, has more than half a century of industrial operation and is one of the best performing technologies for desalting brackish water and sea water so far. Coupling this with the ability to handle a wide range of water sources makes it a strong candidate to tackle current and future water shortage problems. Alongside the advancements in other aspects of RO technology, the development of membrane materials has undeniably made RO desalination more economic by increasing performance and efficiency. Nevertheless, the search for multifunctional membrane materials that offer higher permeability, high ion and organic contaminant rejection, and operational robustness is still ongoing.

At the same time, research is expected to benefit the desalination industry by lowering the energy cost and membrane area required; simplifying pre-treatment processes; providing lower membrane maintenance costs; potentially achieving single pass RO desalination; and increasing plant capacity.^{55,56} Therefore, combining the advantages of multiple desalination technologies in desalination will become the future research and developments efforts.^{57,58} Such as,

- (1) Combining the RO and ED process. As shown in Fig. 1.23, two extreme configurations of the generic design, representing designs with Seawater Diluate Ratio (SDR), which $SDR = 0$ and $SDR = 1$.⁵⁹

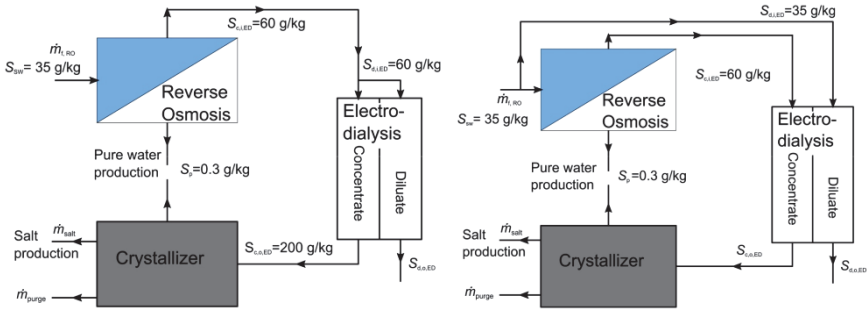


Fig. 1.23. Flow diagram of a RO-ED-crystallizer with (a) SDR = 0 (no seawater feed in ED dilute) and, (b) SDR = 1 (all of the ED dilute is from seawater feed).⁵⁹

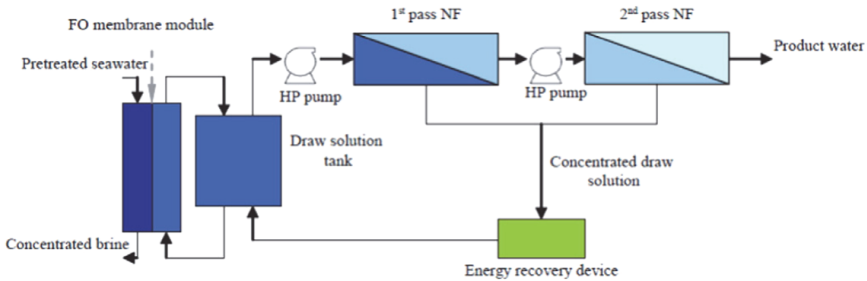


Fig. 1.24. Schematic diagram of hybrid FO-NF-NF seawater desalination process.¹⁴

- (2) Integrated RO and NF desalination processes. Integrating RO with NF desalination process may increase the complexity and cost of desalination plant. However, NF pretreatment has shown effectiveness in removing divalent ions and reducing osmotic pressure from the RO feed water, and integrated NF with RO could join the advantages from both kinds of membranes.
- (3) Integrated NF and FO desalination processes. In an FO-RO desalination system, the role of FO pass is drawing water from seawater, and the RO produced freshwater by concentrating the diluted FO draw solution. A FO-NF-NF system is shown in Fig. 1.24, water was first driven from seawater to draw solution through the FO membrane and then the two-stage NF process removed salt from diluted draw solution to form fresh water.¹⁴

- (4) Integrated NF and ED desalination processes. ED technology also has potential to concentrate the brine of RO, NF-RO and NF-RO-multi-effect distillation (MED) processes to become suitable feed for membrane electrolysis for desalination.¹⁴
- (5) Integrated RO, NF and multistage flash (MSF) desalination processes. A NF-RO-MSF desalination process as shown in Fig. 1.25, in which NF membranes were used to remove scale forming ions from seawater, allowing higher top brine temperature operation of the MSF processes. Not only was the water productivity improved but also the service life of cascade staging of MSF distillers was extended.¹⁴

Using desalination technologies driven by renewable energy sources is a viable way to produce fresh water in many locations today. Combining these renewable energy advances in water desalination technologies has unique synergies in regions where desalination

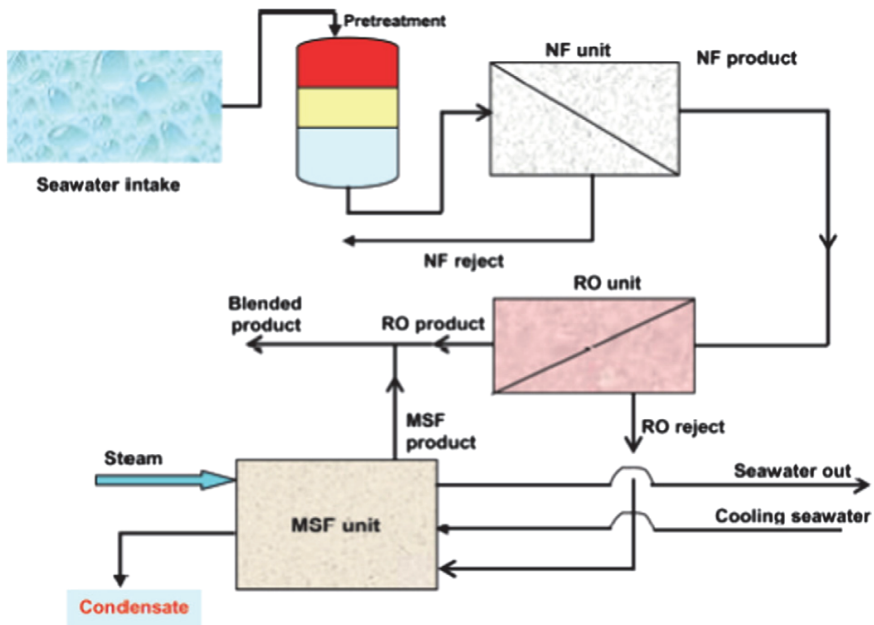


Fig. 1.25. Schematic diagram of hybrid NF-RO-MSF seawater desalination process.¹⁴

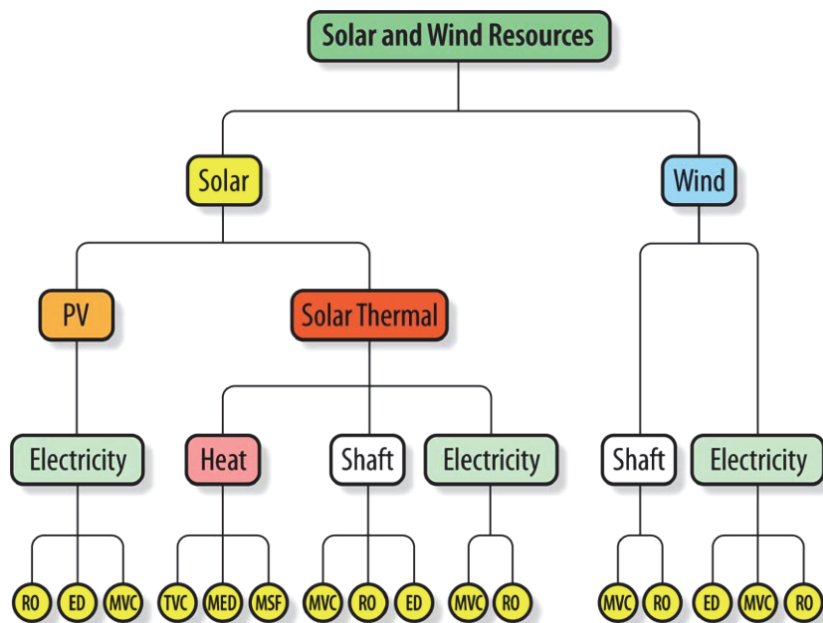


Fig. 1.26. Possible combination of solar and wind systems with desalination processes.¹⁶

is most needed.⁶⁰ Figure 1.26 shows the possible combination of solar and wind systems with desalination process.

With better water resource management, improved efficiencies, and conservation are vital for moderating demand and improving availability, it is our belief that improving the science and technologies of water desalination can help provide cost effective and robust solutions.

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