

Appendix A

Desalination Technologies

Distillation

The evaporation of water molecules from a brine can be accelerated by heating the brine to its boiling point—100° C. at normal atmospheric pressure. Boiling occurs at lower temperatures if the vapor pressure over the brine is reduced. Since reducing the vapor pressure is less costly than adding heat to the brine, commercial distillation processes usually involve boiling the brine at successively lower vapor pressures without adding heat. Most volatile substances (e. g., many potentially toxic synthetic organics) and a very small amount of salt in the brine will also be carried along with the water vapor (91).

Condensation of the water vapor to “distilled” water occurs when the energy required for vaporization—the ‘heat of vaporization’—is given up by the water vapor when it comes in contact with a cooler surface. To maximize the efficiency of the distillation process the heat given up during condensation is used to heat incoming feed water, or to reheat the remaining brine. This can be done by condensing water vapor on one side of a metal surface and simultaneously transferring the heat given up during condensation to the cooler brine (or feed water) on the other side of the metal surface.

Distillation plants typically have very high capital costs. With the exception of solar stills, plant designs are typically quite complicated. To withstand exposure to high temperatures, and corrosive brines and chemicals, high-cost metals, such as titanium and copper-nickel alloys, are typically used. Operating a distillation plant (except solar stills) and attendant pretreatment systems requires highly skilled workers, continuous monitoring of plant operating conditions, and maintenance every few months. Otherwise, major and very costly breakdowns can easily occur.

Four major processes used to distill water on a commercial or semi-commercial scale are discussed below.

Multiple-Effect (ME) Evaporation

In this process incoming feed water is heated and then passed through a series of evaporators, or “effects.” In the first effect, water vapor is given off by the hot brine, which lowers the brine temperature. The brine is then transferred to the second effect, where it comes in contact with one side of a series of tubes. The water vapor produced in the first effect is also transferred to the second effect where it condenses on the other side of the tubes. The heat produced during condensation is trans-

ferred back to the brine, thereby boiling and further evaporating the brine in the second effect. The vapor pressure in each succeeding effect is lowered to permit boiling and further evaporation at successively lower temperatures in each effect.

ME desalination was the first seawater distillation process to be developed for large-scale applications (2). In fact, by 1900 simple 2- to 4-effect stills were available for commercial use (91). In 1958 a plant having five 6-effect units with a total capacity of 2.5 million gallons per day (mgd) was constructed. This was the largest plant of this type built. An average ME plant recovers a volume of freshwater that is between 40 percent to 65 percent of volume of salty feed water. The remaining concentrate is discharged as waste (77). ME units account for about 5 percent of the world’s distillation capacity and have been used very successfully on many Caribbean islands (33).

Multi-Stage Flash (MSF) Distillation

In this process incoming feed water is first heated in a brine heater before it enters the first chamber, or stage. The brine boils violently and a small portion instantaneously “flashes” into water vapor. As the brine passes through successive stages operated at continually lower temperatures and vapor pressures, more and more of the brine flashes into steam. The water vapor produced is then condensed on the outside of tubes conveying incoming brine to the brine heater. The distilled water produced in each stage often passes through each succeeding stage and is allowed to “reflash”; this allows the transfer of additional heat to the incoming feed water.

A typical MSF plant may have 20 to 50 stages. On the one hand, many stages increase the overall efficiency of heat recovery in the plant and decrease its operating costs. On the other hand, more stages increase the capital cost of the plant. In most recently built MSF plants, 50 to 75 percent of the waste concentrate from the last stage is mixed with the incoming feed water to increase the heat recovery and decrease the amount of water needing pretreatment. Unfortunately, this also increases the corrosion and scaling (i. e., precipitation of inorganic minerals) in the plant due to the increased salt concentration in the circulating brine. An average MSF plant recovers a volume of fresh water that is between 25 percent to 50 percent of the volume of incoming feed water (77).

MSF distillation was developed in the late 1950s; the first commercial plant was built in 1957 in Kuwait (77).

In the early 1960s a MSF plant was built in San Diego (CA) and moved in the mid- 1960s to our navy base at Guantanamo Bay, Cuba, where it operated for about 20 years. Since the late 1960s MSF plants have dominated the commercial distillation market (91). Because of the significant economies of scale achieved by large-capacity plants, and the extensive design and operational experience gained over the last three decades, MSF plants, found in 55 countries, now account for almost two-thirds of the world's desalination capacity, or about 2 billion gpd. Individual units as large as 10 mgd are now being built. In fact, a MSF multi-plant complex with a total capacity of almost 300 mgd was completed in Saudi Arabia in the early 1980s (33,77).

Vapor Compression (VC)

In the two previous distillation processes reduced vapor pressure over the brine is used to enhance its vaporization. In VC units water vapor is collected and compressed. This compression causes the vapor to condense on one side of a tube wall. The heat given off during condensation is then transferred (through the tube walls) back to the feed water to enhance its evaporation. In this process the major energy input is provided by the compressor, which not only compresses the vapor, but also reduces the vapor pressure in the vaporization chamber. Energy may also be required to heat the incoming feed water during start-up (91).

During World War II the United States performed considerable work on VC for use on ships and at isolated bases around the world. VC units now account for about 2 percent of the world's capacity with unit sizes generally being less than 0.1 mgd. These units are typically diesel-powered and may be used on ships, offshore oil rigs, at remote construction sites, and at resort hotels in water-limited regions of the world (28,33,77).

Solar

Solar distillation units can have many configurations, but the most common one is referred to as a greenhouse still. In this unit saline feed water is supplied continuously or intermittently to a pool of water inside an airtight, glass enclosure, similar to a greenhouse. The black pool bottom absorbs the solar energy and heats the water. Water vapor rising from the brine condenses on the cooler inside surface of the glass. The droplets of water vapor then run down the glass into troughs along the lower edges of the glass which channel the distilled water to storage tanks. After about half of the feed water has evaporated the remaining waste concentrate must be discarded to minimize precipitation of salt.

Ever since the advent of commercially produced glass sheets in the second half of the 19th century, solar stills

have been used in extremely remote, sunny areas of the world. One of the first successful commercial solar stills covering 4,500 sq. meters (48,000 sq. ft.), was built in Las Salinas, Chile, in 1872 and operated for 40 years (17). This still produced 6,000 gpd (18). Over the last two decades about 35 solar stills have been built in a dozen different countries throughout the world (41). Solar stills typically have ratios of capital cost to operating cost of four to one; for most other distillation units this ratio is two to three.

Although solar stills are relatively easy to build and operate, there are few, if any, economies-of-scale associated with larger plants (37). For example, the largest solar stills yet tested have produced only a few thousand gallons of water per day. A well-designed solar still can produce 2 to 4 liters (or quarts) of water per square meter of basin area. Overall costs for water produced by solar stills range from about \$50 to \$80 per 1,000 gallons (77). The Indian Institute of Technology in New Delhi, India has apparently developed a portable still that is about half the cost of similar units now on the market (88).

In the 1960s the Federal Office of Saline Water in the DOI extensively investigated various solar still designs, including glass-covered basins, inflatable plastic basins, tilted wicks and trays, and all-plastic double tubes (72). Although the program was terminated in 1970 when it was concluded that the high capital costs could not be reduced significantly, the program did produce design data that has been used in numerous solar stills built in various parts of the world since 1970 (77).

Solar energy has recently been used to heat water prior to distillation or to provide electricity from photovoltaic cells for other types of experimental and small-scale RO, ED, and distillation plants discussed in this chapter. However, these plants tend to be smaller, more expensive to operate, and must be equipped with auxiliary power sources to operate at night or during cloudy weather. Such systems appear to have potential only in remote, sunny areas of the world (21, 77,88).¹

Reverse Osmosis (RO) (42)

If waters with different salinities are separated by a semi-permeable membrane, "pure" water from the less salty brine will diffuse or move through the membrane until the salt concentrations on both sides of the membrane are equal. This process is called osmosis. With RO, salty feed water on one side of a semi-permeable membrane is typically subjected to pressures of 200 to 500 lb/sq in. for brackish water, and 800 to 1,200 lb/sq in. for seawater. z "Pure" water will diffuse through the

¹The development of desalination units powered by other alternative energy sources (e. g., wind, ocean wave energy, salt ponds, etc.) is in its infancy (8).

²Normal atmospheric pressure is 14.7 lb/sq in.

membrane leaving behind a more salty waste concentrate (91).

About 10 gallons of water will pass through a square foot of membrane each day. The higher the operating pressure, the greater the flow of product water. The percentage of incoming feedwater that is recovered as product water after one pass through an RO module ranges from about 15 to 80 percent; however, this percentage can be increased if necessary by passing the waste water through sequential membrane elements (8). Brackish water RO plants typically recover 50 to 80 percent of the feed water, with 90 to 98 percent of the salt being rejected by the membrane. Recovery rates for salt water RO plants vary from 20 to 40 percent, with 90 to 98 percent salt rejection. The water is usually processed at ambient temperatures.

Membranes, which are usually made of cellulose acetate, aromatic polyamide, polyimide, polysulfones, or thin film composites, can last as long as 7 years depending on the composition of the membrane used and the quality of the feed water. Membranes used for seawater generally have to be replaced every 3 to 5 years. Membranes can be designed to remove particular inorganic and organic contaminants, such as trihalomethanes. Low pressure membranes have decreased the pressure requirements for some RO operations by up to 50 percent. The efficiency of RO operations will undoubtedly increase and costs decrease as membranes are improved. Such improvements may involve increased rejection of salt; increased membrane resistance to compaction, chlorine, and microorganisms; and large-scale production of standardized RO elements. RO is being used increasingly in the emerging area of nanofiltration of water.

Reverse osmosis can remove from brines not only dissolved solids, but also organic material, colloidal material, and some microorganisms. RO is typically used for brackish water with salt concentrations ranging from 100 to 10,000 ppm; however, membrane developments over the last decade have made it economically possible to use reverse osmosis for seawater (7,77). RO consumes only one-third to one-half of the energy required for MSF distillation (7,12,61). In addition to using RO for desalinating drinking water, it is also used extensively by industries and municipalities to treat feedwater (including water softening), and to treat wastewater prior to disposal or reuse.

Membranes are manufactured in three basic configurations: half-inch, hollow tubes; hollow, hair-like fibers; or several alternating layers of membranes and "spacer" materials that are rolled into a spiral configuration, or stacked in a sandwich form. The latter two configurations are now the most commonly used for commercial applications (77). The membranes are

sealed into tubular plastic, pressure vessels, called elements. The elements used for most plants measure 4 to 12 inches in diameter and 1 to 4 feet in length, and are assembled in parallel and in series in steel racks.

RO plants usually consist of a series of standard-sized modules each with a capacity of about 2,000 gpd (77). Plant design, construction, and operation are all relatively straightforward, especially for brackish groundwater. Pretreatment of the incoming feedwater is usually necessary, especially for seawater; otherwise, clogged membranes will require more frequent replacement, thereby significantly increasing the expense of the operation.

During the first few thousand hours of operation, the processing capacity of a RO plant may decrease by up to 25 percent due to membrane compression (i. e., densification) at higher pressures, and/or membrane deterioration. Another 20 percent of the capacity can be lost due to membrane fouling. Most of this latter capacity can be regenerated by periodically (e. g., every 1,000 hours of operation) flushing a hot cleaning solution through the filter elements (1).

The feasibility of RO was demonstrated in the laboratory in the mid-1950s and field tested in the mid-1960s at a seawater conversion plant near San Diego, CA. The first municipal brackish water RO plant built in Greenfield, IA, in 1971 had a capacity of 150,000 gpd (47). The development and demonstration of RO was heavily supported by the Federal desalination research program during this early period and throughout the 1970s. In fact, most desalination experts agree that without this Federal support RO would certainly not have been developed to its current level of sophistication.

There are now about 1,750 major RO plants in over 63 countries with a combined capacity of about 700 m_gd.; just over 35 percent of this capacity is in the United States (86). In fact, Florida alone has about 70 reverse osmosis plants (larger than 25,000 gpd) that are supplementing existing supplies of drinking water. A "typical" municipal RO plant has a capacity of between 0.2 and 0.6 mgd (77). Smaller RO units with capacities of 10,000 to 70,000 gpd are also now being manufactured for various commercial and military uses. Low-capacity under-the-sink units are being sold for point-of-use water treatment for the home.

Electrodialysis (ED)

ED is a process that uses a direct electrical current to remove salt, other inorganic constituents, and certain low molecular weight organics from brackish water with concentrations of dissolved solids up to 10,000 ppm. ED tends to be more economical than RO at sa-

linities of less than 3,000 ppm, and less economical than RO at salinities greater than 5,000 ppm. Seawater ED is not yet commercially available (2,65).

With this technique several hundred flat, ion permeable membranes and water flow spacers are vertically assembled in a stack. Half of the membranes allow positively charged ions, or cations, to pass through them. The other half-anion-permeable membranes—allow negatively charged ions to pass through them. The anion permeable membranes are alternately placed between the cation-permeable membranes. Each membrane is separated from the adjacent membrane in the stack by a polyethylene flow spacer. This assemblage of one cation membrane, a flow spacer, one anion membrane, and another flow spacer comprise the cell pair, which is the basic building block of an ED cell.

An electrical current (powered by an external d.c. electric power source) is established across the stack by electrodes positioned at both ends of the stack. Brackish water is pumped at low pressures (e. g., 50 to 70 lbs/sq. in.) into the 0.04-inch flow spacers between each membrane. The cations pass through the cation-permeable membranes and anions through the anion-permeable membranes, thereby concentrating between each alternate pair of membranes. Between each set of membrane pairs adjacent to the concentrating compartments, the brackish water is partially desalinated. ED will not remove uncharged molecules (55).

Partially desalted water is passed through additional ED stages until the desired desalination is achieved. Typical salt removal varies from 40 to 50 percent for a single stage plant (i.e., one pass through a single stack) and, 65 to 75 percent and 82 to 88 percent removal for 2- and 3-stage plants, respectively (65). The amount of electricity required for ED, and therefore its cost, increases with increasing salinity of the feed water. ED systems typically operate more efficiently at elevated temperatures of up to 110 degrees F (91).

Scaling or fouling of the membranes, the most common problem encountered with ED, is prevented in most ED units built since the mid- 1970s by operationally reversing the direction of the electrical current through the stacks at 15- to 30-minute intervals. This process is called electrodialysis reversal, or EDR, and is an automatic, self-cleaning electrodialysis process. Polarity reversal reverses the flow of ions through the membranes, so that the spaces collecting concentrated brine begin collecting less salty product water. Alternating valves in the water collection system automatically direct the flow in the appropriate direction depending on the direction of the current. Typical freshwater recovery rates for EDR now range from 80 percent to 90 percent of the feedwater volume (65).

ED plants are constructed and operated in much the same way as RO plants. Similarly, some pretreatment

may be required; however, EDR typically requires much less pretreatment of incoming feed water than other desalination processes. If scaling and/or clogging of the membranes becomes a problem, effective chemical cleaning is achieved by circulating a solution through the membrane stacks. The membrane stacks may also be disassembled and the membranes cleaned by hand. Although this is time consuming, it avoids the frequent replacement of membranes. Under proper operating conditions ED membranes are guaranteed for up to 5 years, but may have an effective life of 10 years or more (55,77,91).

Extensive laboratory work on ED occurred in the 1930s and 1940s. It was commercialized for desalting brackish water supplies in the 1950s using sheet membranes made from ion-exchange resins. At this time ED has significant economic advantages over distillation for desalinating brackish water. ED was first used in the United States in 1958 to supply freshwater to Coalinga, California. Four years later a 650,000 gpd plant was constructed in Buckeye, Arizona. Several hundred ED plants with a combined capacity of about 140 mgd (86) are now operating in over two dozen countries where they are used primarily for industrial purposes and for municipal drinking water. A typical ED plant can range in size from 0.05 to 0.5 mgd. The largest installation is an 8 mgd plant in Iraq (55,65,77,91).

One American company (Ionics, Inc.) continues to dominate the market for ED units throughout the world. However, several Japanese firms have been involved in further developing the ED process. The U. S. S. R., China, and India have also been experimenting with the ED process and various unit designs (77).

Ion Exchange

In this process undesirable ions in the feed water are exchanged for desirable ions as the water passes through granular chemicals called "ion exchange resins." For example, cation exchange resins are typically used to remove calcium and magnesium ions in "hard" water. However, special resins are available for adsorbing organics. A 1981 survey of public water supply systems by the American Water Works Association found almost 50 systems that use IX for water softening. Many homeowners also have IX units for softening water prior to use. For industries requiring extremely pure water, ion exchange resins are often used after RO or ED to "polish" the water by removing specific ions from water and wastewater.

Treating water with ion exchange resins is relatively simple to do. The primary cost is associated with periodically regenerating or replacing the IX resins. The higher the concentration of dissolved solids in the feed water, the more often the resins will need to be replaced

or regenerated with other chemicals (e. g., strong acids, bases, or high concentration chemical solutions). Also, any organics in the water may foul some resins, thereby reducing their exchange capacity. Reliable cost estimates for different IX processes are not widely published, but appear to be very ion- and process-dependent (55). In general, IX becomes competitive with RO and ED only in treating relatively dilute solutions containing a few hundred ppm of dissolved solids. IX is rarely used for salt removal on a large-scale (e. g., for municipal water treatment).

The only municipal water treatment plant in this country using IX for treatment other than water softening was built in Burgettstown, Pennsylvania, in 1972. In this case, the 500,000-gpd plant processes drinking water supplies that have been contaminated by acid mine drainage (91). IX units can also be used where small amounts of freshwater are needed, such as on spacecraft.

Freeze Desalination

When salty water freezes, the ice crystallizes from pure water leaving the dissolved organic and inorganic solids (e.g., salt) in liquid pockets of high salinity brine. Traditional freezing processes involve five steps: precooling of the feed water, crystallization of ice into a slush, separation of ice from the brine, washing the ice, and melting the ice. Although freshwater can be obtained quite easily from ice where seawater freezes naturally, the engineering involved in constructing and operating a freeze desalination plant is quite complicated.

Freeze desalination has the potential to concentrate a wider variety of wastes streams to higher concentrations with less energy than any of the distillation process discussed above (55). In fact, the energy requirements for freezing and reverse osmosis are comparable. Pretreatment of incoming feed water is not necessary and corrosion is much less of a problem with freezing

due to the low operating temperatures. Some equipment development required for freeze desalination has occurred over the last 30 years, and the technical feasibility of freeze desalination has been established; however, a considerable amount of research and development still remains before this technology can be used commercially on a large scale (34).

One variation of the freezing concept with some potential involves spraying seawater, or contaminated freshwater, into the air when winter temperatures fall below 29° F for significant periods of time. The partially frozen spray is collected in a reservoir where the pure ice accumulates and the unfrozen saltwater drains back into the sea. Costs are likely to run about \$1.50 to \$3.00 per 1,000 gallons, even for small scale applications (i. e., less than 1 mgd). This variation on freeze desalination can only be used in colder winter climates (73). However, very recent work using low energy refrigeration systems may allow use of this technique in any climate, with preliminary cost estimates of \$1.50 per 1,000 gallons for feed water with a solids concentration of 1,000 ppm and about \$2.00 per 1,000 gallons for seawater (74).

New Concepts

There are several new concepts and/or variations on existing concepts that may have some potential. Among these are: hybrid desalination plants that optimize the use of capital and energy resources by combining various desalination processes (e. g., RO and distillation); computerization of desalination operations; three-stage ion-exchange "Desal" process (55); "Delbuoy" concept that uses ocean waves to power RO equipment; "Puraq" liquid-liquid extraction of pure water using a polymeric solvent; "Gravacutron" vacuum distillation process; distillation units coupled with ocean thermal energy conversion plants, etc. The potential of these concepts for economically purifying water is not known.