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ABSTRACT

This publication provides a simple explanation of how various processes convert sea or brackish water to fresh water. Included are descriptions of the membrane processes (reverse osmosis, electrodialysis, transport depletion, and piezodialysis); the distillation processes (multistage flash distillation, vertical tube distillation, multieffect multistage distillation, vapor compression distillation, and solar humidification); the crystalization processes (vacuum freeze-vapor compression, secondary refrigerant freezing, eutectic freezing, and hydrate formation); and a chemical process (ion exchange). (BB)

THE A-B-C OF DESALTING

U.S. DEPARTMENT OF THE INTERIOR
Office of Water Research and Technology
Technology Transfer
Washington, D.C.

This publication has been prepared to provide a simplified explanation of how various processes convert sea or brackish water to fresh for the purpose of conserving and increasing the water resources of the nation.

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THE WATER PROBLEM

THE UNITED STATES is currently withdrawing fresh water at a rate of approximately 360 billion gallons a day—almost three times the rate of 30 years ago. Population growth and the increasing need for fresh water for municipal, industrial, and agricultural uses indicate there will be no letup in the increasing demand for water in the years to come.

These factors account for the concern over water shortages that exist now in some areas of the country and over the more serious shortages that are projected for the near future. Many localities are forced to impose restrictions on the use of water when rainfall is only slightly below normal. It has been apparent in recent times that, unless new sources of fresh water are developed, more and more communities will have to face up to water shortages. The Federal Government is sponsoring many programs to develop and conserve this important resource in order to ensure an adequate supply of fresh water for our present and future needs. Because three-fourths of the earth's surface is covered by salt water, it is obvious that some of the water shortages could be eliminated by development of effective means of obtaining fresh water from oceans and other bodies of saline water.

The Department of the Interior has been conducting a research program for the development of processes for economically converting saline water into fresh water since 1952.

There are many ways to produce fresh water from saline sources, but to do it at low cost is extremely difficult. The commercial price of fresh water is generally very low. To be economically feasible, fresh water obtained from sea water must be produced at a cost that is comparable to the cost of water from alternative sources of supply.

In some of the more arid areas of the world, natural fresh water is not available in sufficient quantities to meet minimum demands, and in some cases it is not available at all. Desalting plants now in use in arid locations range in capacity from a few thousand to 40 million gallons per day. These plants produce a combined total of more than 525 million gallons of fresh water daily. However, the cost of water produced by these plants ranges upward from 85¢ per thousand gallons, except where fuel is available at very low cost.

Several factors influence the cost of water produced by desalting plants. They include the size of the plant, the cost of energy, and the concentration of salt in the water being demineralized.

THE CONVERSION PROCESSES

Conversion Processes

Membrane:

Reverse Osmosis	Transport Depletion
Electrodialysis	Piezodialysis

Distillation:

- Multistage Flash Distillation
- Vertical Tube Distillation
- Multieffect Multistage Distillation
- Vapor Compression Distillation
- Solar Humidification

Crystallization:

- Vacuum Freezing-Vapor Compression
- Secondary Refrigerant Freezing
- Eutectic Freezing
- Hydrate Formation

Chemical;

- Ion Exchange

SALINE-WATER CONVERSION can be accomplished in many ways. Some methods have been known in concept for centuries while others have been developed only in recent years. The Office of Water Research and Technology has seriously studied the development of fourteen different conversion processes, and it sponsors a continuing research and development program to discover and develop new methods. Some processes are now being used commercially, some have progressed to the pilot-plant stage of development, and others are still under study in laboratories.

The effectiveness of the various processes varies widely insofar as cost and rate of conversion are concerned. The major cost considerations are the capital investment, the cost of energy used in the conversion process, and the cost of operating and maintaining the conversion plant. There are variations in the importance of each of the cost factors, just as there are variations in the conversion-process requirements.

MEMBRANE PROCESSES

THIS SECTION PRESENTS background information to aid in understanding the four membrane conversion processes discussed below There are a number of important differences between the four processes; however, they have in common the use of a thin. film-like sheet, or membrane. In general, a membrane may be considered to be a selective separator—some substances pass through it relatively freely under certain conditions but for other substances the membrane acts as an effective barrier.

The application of mebrane processes to brackish water presents a problem not usually associated with sea-water conversion. The chemical composition of sea water is relatively constant, whereas that of brackish water varies greatly. Variations in the mineral content of the brackish water require that a membrane unit be designed for the particular water to be demineralized, or pretreatments be used. For example, the amount and type of constituents present influence the pretreatment needed, scale-forming tendencies, limits in brine concentration, and number of stages required.

Ions

Ordinary salt is the principal solid dissolved in sea water. It is a good example of an ionic substance. Salt, or sodium chloride, is made up of charged atoms (ions) of sodium and chlorine. The electric charge is positive for the sodium atom and negative for the chlorine atom. Electrically charged atoms behave differently from uncharged atoms and are called ions. The sodium ion is given the symbol Na^+, and the chloride (from chlorine) ion, the symbol Cl^-. In the crystal form, sodium and chloride ions arrange them-

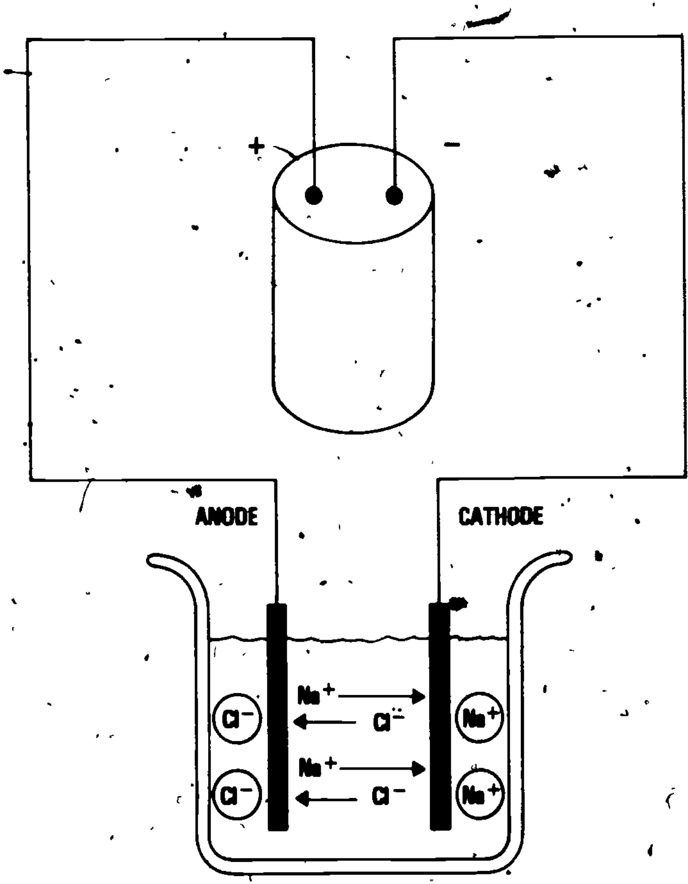


Figure 1

selves alternately in a three-dimensional arrangement called a crystal lattice.

When salt is placed in water, the ions disperse among the water molecules.

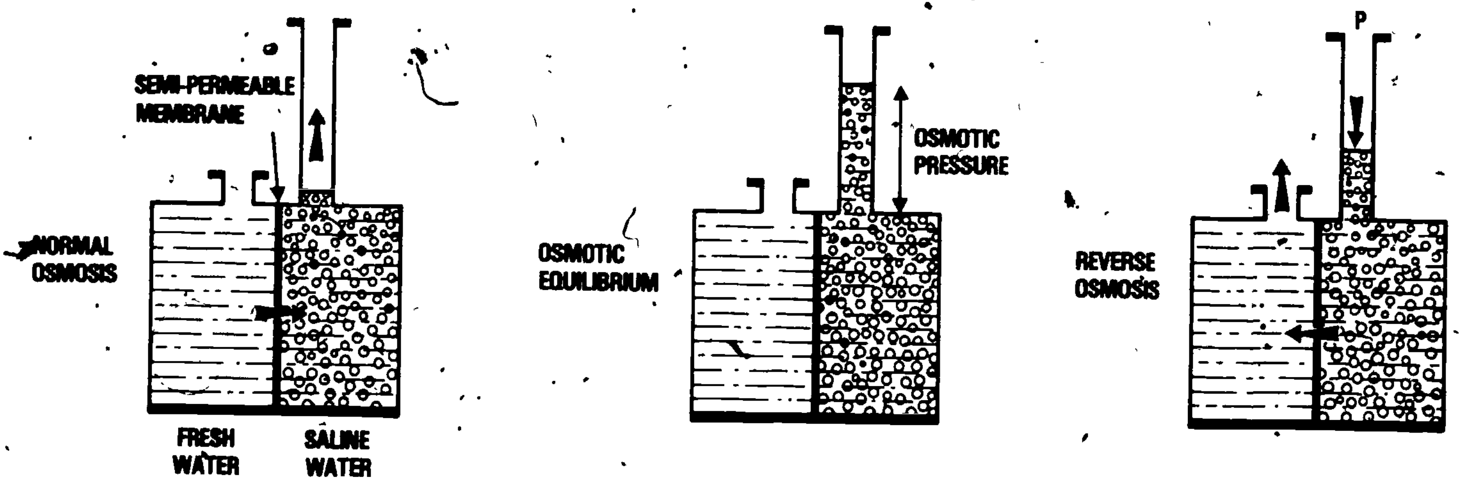
Ions and Conductivity

Three of the four membrane processes described here depend on the electrical charge of ions. **Figure 1** shows a simple demonstration of the effect of an electrical current on an ionic solution. If two metal electrodes are placed in a vessel of very pure water water and connected to a battery, there will be only a very small flow of current. This is because water exists mainly as H_2O molecules which have no electrical charge. If an ionic substance, such as sodium chloride, is added to the water, a much larger current flows. The current is carried by the electrically charged ions which migrate toward the electrode of opposite charge. The sodium ions, Na^+, are attracted at the negative electrode (cathode) and the chloride ions, Cl^-, are attracted to the positive electrode (anode). This effect, called ion transport, obviously offers promise for desalting if the equipment can be designed to operate efficiently.

REVERSE OSMOSIS

When pure water and a salt solution are on opposite sides of a semipermeable membrane, the pure water diffuses through the membrane and dilutes the salt solution. This phenomenon is known as osmosis. Because of the difference in salt concentration, pure water flows through the membrane as though a pressure were being applied to it. The effective driving force causing the flow is called osmotic pressure. The magnitude of the osmotic pressure de-

Figure 2



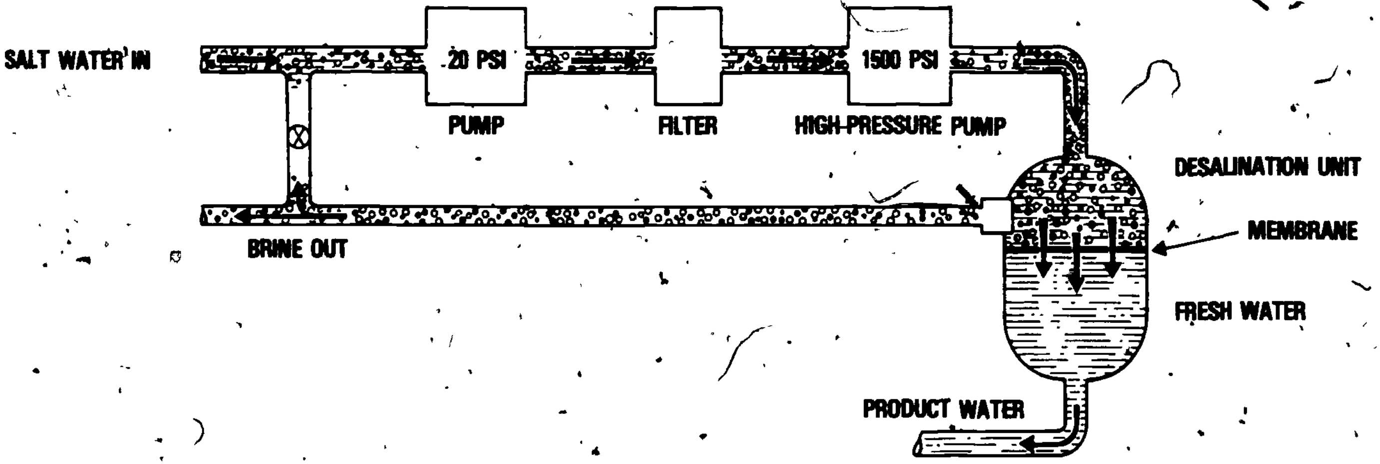


Figure 3

pends on the concentration of the salt solution and the temperature of the water. By exerting pressure on the salt solution, the osmosis process can be reversed. When the pressure on the salt solution is greater than the osmotic pressure, water diffuses through the membrane in the opposite direction to normal osmotic flow.

The principle of reverse osmosis is illustrated in **figure 2**. It can readily be seen how this principle can be applied in the conversion of saline water.

A diagram of the reverse-osmosis process is shown in **figure 3**. The salt water is first passed through a filter where suspended solids that would foul the membranes are removed. The salt water is then raised to operating pressure by a second pump and then introduced into the desalination unit. A portion of the water permeates the membranes and is collected as product water at the bottom of the unit. The brine is discharged at the top of the unit.

Process Designs

Operating plants carry out the reverse-osmosis principle in several different process designs such as the plate and frame, tubular, spiral-wound membrane module, and hollow-fiber designs. All are based on the common principle that the membrane, a flexible plastic film usually no more than 4 to 6 mils in thickness, must have a firm support to withstand the very high pressure drop across it. The preferred materials currently being used for membranes in these process designs are cellulose acetate and polyamides which have been specially processed to make them reject salt and at the same time pass water at a reasonable rate. Research is underway on the development of a number of new noncellulosic membranes with superior properties. It is anticipated that these new membranes will eventually supplant current materials for a number of desalting applications.

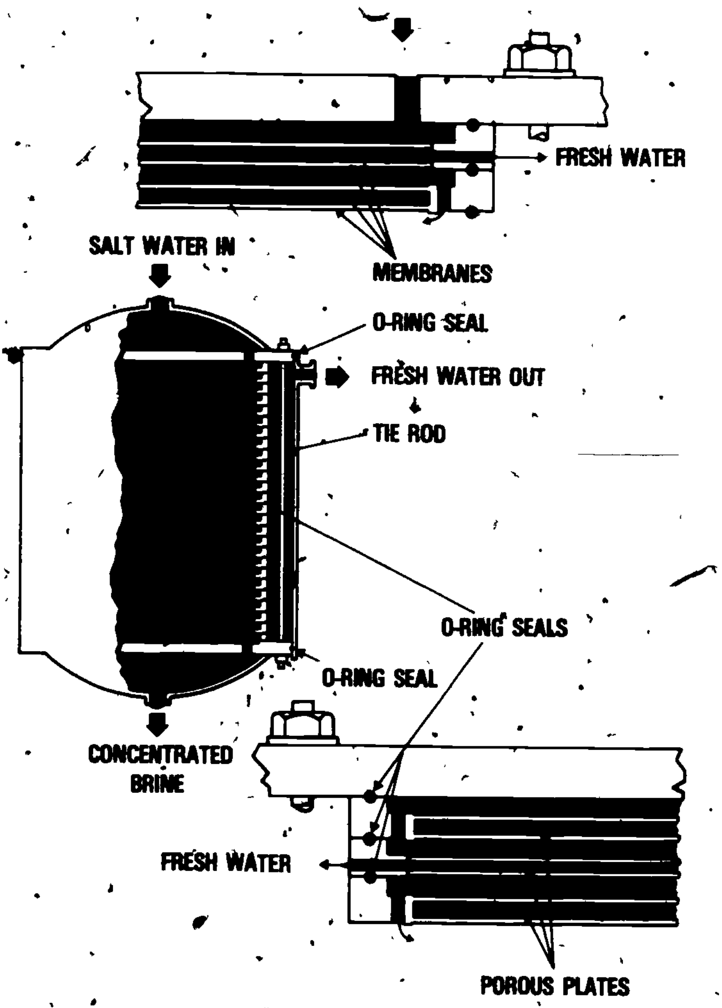


Figure 4

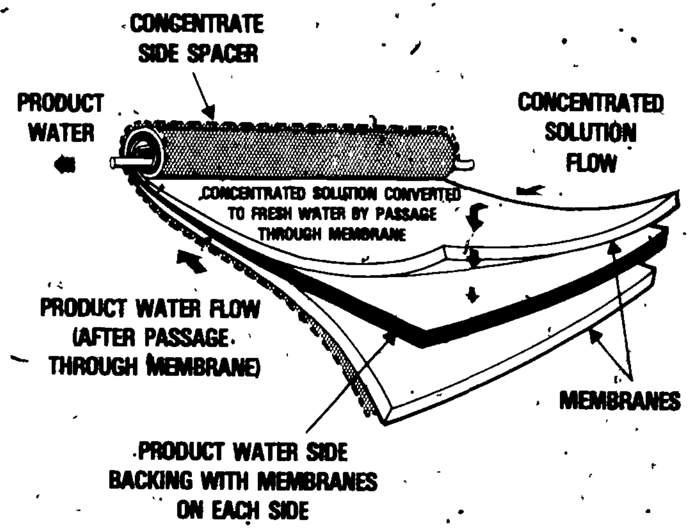


Figure 5

Plate and Frame

This design makes use of a rigid plate with the membranes mounted on opposite sides and sealed to the plate. The pressure is applied to the salt water on the outer sides of the plate, and the product water is forced through the membranes into the interior of the plate, which is at low pressure. The interior of the plate must therefore be either porous or have hollow channels through which the product water can flow to a collecting point where it passes to the outside of the pressure vessel. Plate materials may consist of solid plastic plates with grooved channels, porous fiberglass materials, or reinforced, porous paper. **Figure 4** illustrates the process with circular plates inside a cylindrical vessel.

Spiral-Wound Membrane Module

This process design is so named because the membrane is wound into a spiral unit before being placed into the pressure vessel. This has the advantage that the membrane and the support between the high- and low-pressure sides of the membrane can be formed into an ordinary commercial pipe so that a special pressure vessel is not required. This spiral is formed as shown in **figure 5.** One may think of the spiral as being a flat envelope made up of the membrane with three sides sealed and one end left open to transfer the product water to a collector tube attached at the open end. Within the envelope is placed a plastic or glass fabric material which is capable of withstanding the high pressures on the outside of the envelope but is sufficiently porous to carry the product water to the collector tube. To form the spiral, the envelope is wrapped into a roll around the central product-collecting tube. A coarsely woven fabric is rolled with the membrane envelope to form a path for the salt water to flow through the module from end to end over the membrane surface. A schematic of an operating unit is shown in **figure 6.**

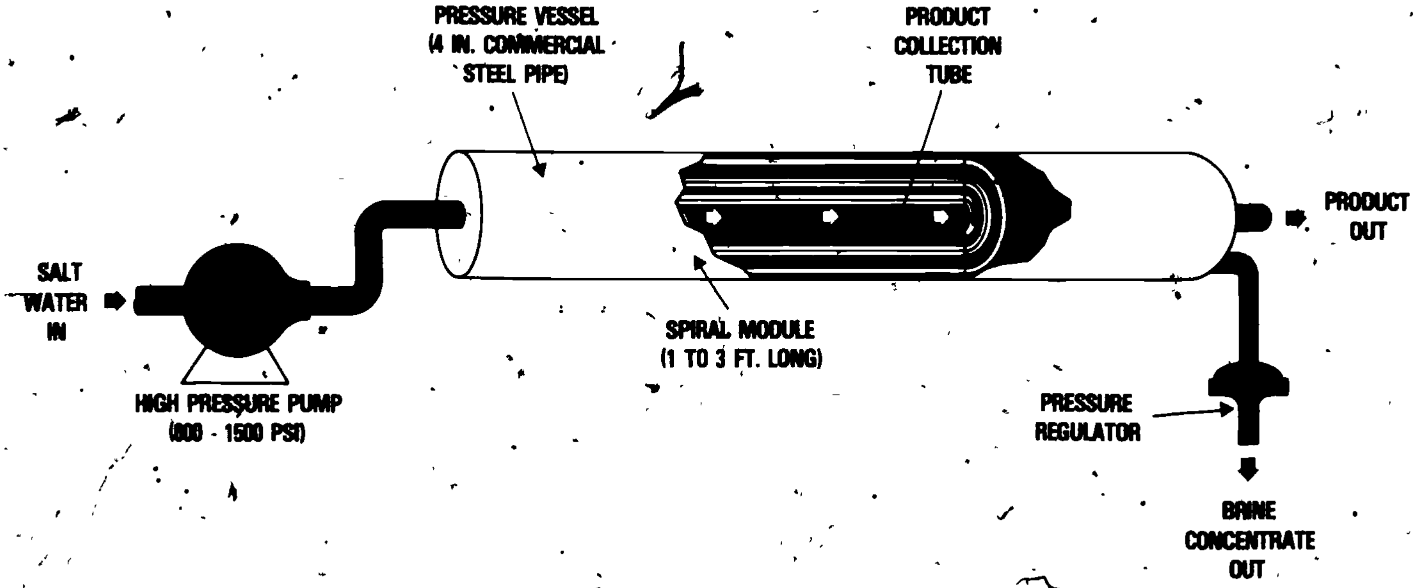


Figure 6

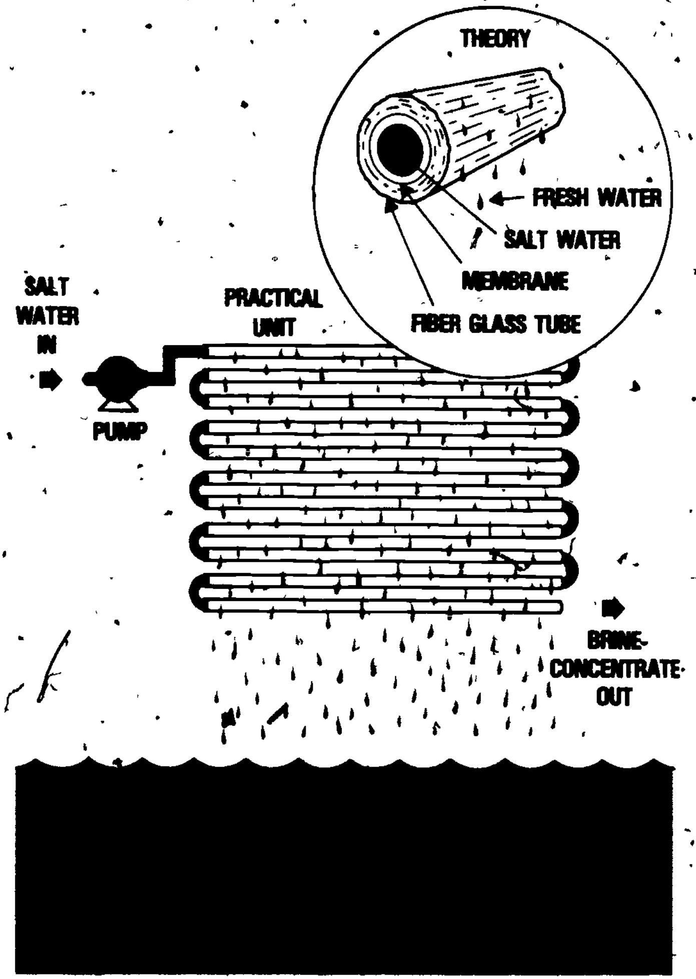


Figure 7

Tubular

The tubular design combines two functions in one in that it uses the surface of the tube as a support for the membrane and the tube wall as a pressure vessel. Normally, the membrane is placed on the inner wall of the tube, and the salt water, under pressure, flows inside the tube. Product water passes through the membrane to the tube wall, where arrangements are made to transfer the product water, now at low pressure, to the outside of the tube. This may be done by using a tube which is porous over its full length, permitting direct flow of the product water to the outside of the tube. When a solid tube is employed, small holes are placed at intervals along the tube, and a porous fabric material is placed between the membrane and the pressure tube to provide a path for the product water to the outlet parts. Porous fiber-glass tubes ½ inch in diameter are a popular material for this purpose. **Figure 7** illustrates the operation of the tubular process.

Hollow Fiber

Newest of the process designs is the hollow fine fiber. Modern technology has made possible the production of hollow plastic fibers from membrane materials which may measure from 25 to 250 microns in outside diameter (approximately 0.001 to 0.01 inch). These fibers fabricated from cellulose acetate or polyamide, have the unique feature that, in these very small diameters, they can withstand enormous pressures and can, therefore, provide their own pressure support. Closely packed fibers of this type can also provide a very large membrane surface area in a small volume of pressure-vessel. Product flow for a square foot of fiber surface is less than for the same area of flat membrane, but the difference in area within a given volume compensates for this difference in flow rate. In a hollow-fiber process, the fibers are placed in a pressure vessel with one end sealed and the other end extending to the outside of the vessel through a plastic seal in which the fibers are embedded. The salt water, under pressure, is on the outside of the fibers, and the product water flows inside the tiny fibers to the open end on the outside of the vessel. **Figure 8** illustrates the operation of the process.

Advantages and Limitations

Some of the important advantages of the reverse-osmosis process are:

1 Low energy consumption. Because no change of phase is involved, the only energy consumed is the electrical energy needed to drive the pumps.

2. The processing equipment is relatively simple, resulting in low equipment costs.

3 The operation of the process at normal temperatures minimizes scale and corrosion problems.

At the present time this process is limited in that only brackish water concentrations can be handled efficiently. However, research and development is being conducted to increase its effectiveness for sea water.

Memb[illegible]elopment

Th[illegible]ssful application of the reverse-osmosis process depends on membrane development. In general, development of membranes is aimed at obtaining long life with high rates of fresh-water diffusion through the membrane at a reasonable cost.

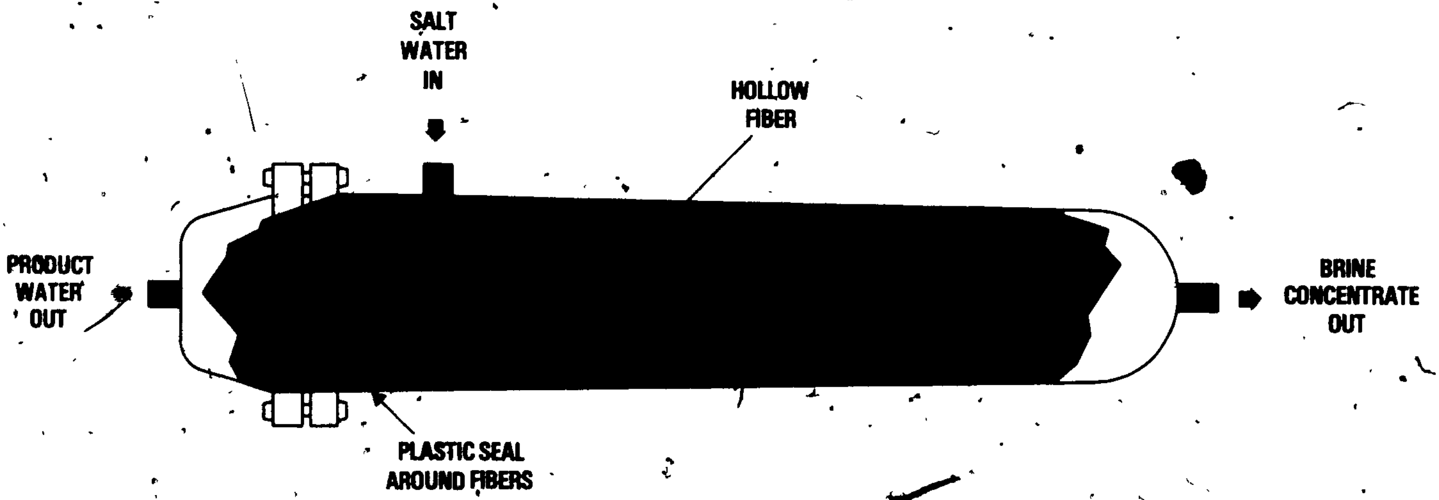


Figure 8

ELECTRODIALYSIS

From a standpoint of research and development accomplished to date, electrodialysis is the most advanced of the membrane processes. An electrodialysis conversion assembly is essentially a cell containing two different types of ion-selective membranes. One of the membrane types allows passage of positive ions, or cations, and the other allows passage of the negative ions, or anions. The electric current imposed on the electrodialysis cell provides the driving force for the ions. A basic electrodialysis cell is shown in **figure 9.** The cation-permeable membrane allows passage of the postive sodium ions, and the anion-permeable membrane allows passage of the negative chloride ions, leaving fresh water between the membranes.

The amount of electric current required in a unit which contains many sets of membranes between the electrodes depends on the amount of dissolved salt to be removed. Therefore, the cost of the energy consumed in the process depends on the concentration of dissolved minerals in the feed water. The relationship between electric current requirements and dissolved salts is the main reason that electrodialysis is more economical for brackish water conversion. However, if the cost of membranes and processing equipment can be reduced sufficiently, electrodialysis may become economically feasible for sea-water conversion. Research is currently being conducted to investigate the feasibility of operating the electrodialysis process at elevated temperatures. High temperatures reduce the electrical resistence of the electrolyte and lower electric power requirements. High-temperature operation shows promise of reducing power requirements sufficiently to make electrodialysis attractive for sea-water conversion.

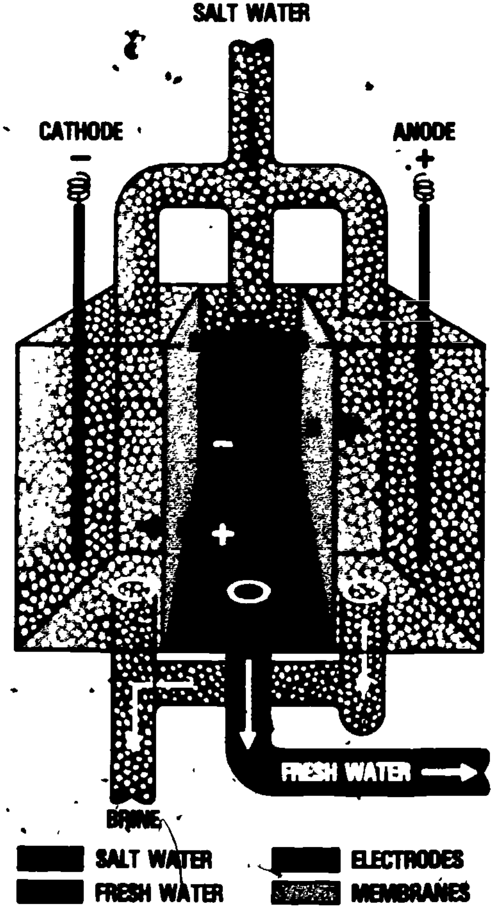


Figure 9

Membrane Development

The membranes used in an electrodialysis unit are produced by chemically treating a polymeric material such as polystyrene or polyethylene. A number of fabrication techniques have been investigated. Some of the techniques give low cost membranes, while others give membranes of longer life and high cost. The development program is directed toward obtaining membranes that give the best compromise between life, ion selectivity, and hydraulic and electrical characteristics.

TRANSPORT DEPLETION

Transport depletion is a variation of the electrodialysis process. In this process, nonselective membranes are used in place of the anion permeable membranes. The anion-permeable membranes tend to deteriorate more rapidly under operational condititons, and their elimination represents a considerable saving in membrane costs, but power costs are increased.

A transport-depletion cell is shown in **figure 10.** Saline water enters at the top and passes into two compartments separated by a non-selective membrane and each bounded by a cation-permeable membrane. The passage of an electric current causes cations to pass through the cation-permeable membranes and anions to pass through the nonselective membrane. The net result is that one compartment becomes depleted of ions and the other becomes enriched. The ion-depleted product water and the ion-enriched brine are removed at the bottom.

The process would be similar if anion-permeable membranes were used instead of the cation-permeable membranes. However, the operational difficulties favor the elimination of anion-permeable membranes.

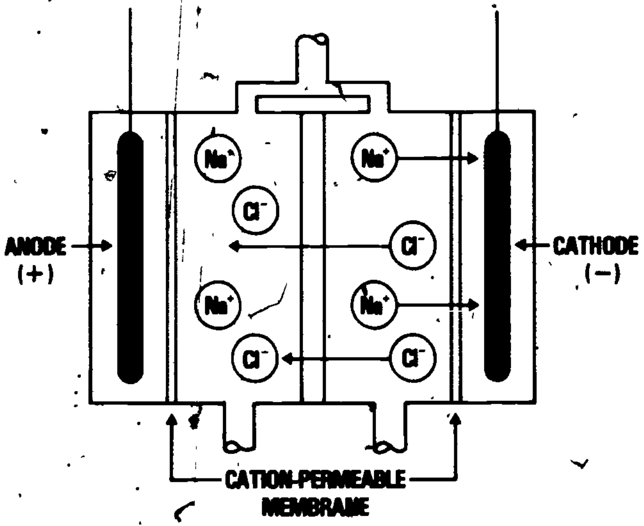


Figure 10

Process Characteristics

The advantages and limitations of this process in general are those that apply to electrodialysis. As in the electrodialysis process, the success of transport depletion is closely tied to the membrane development program. The power consumed in the transport depletion process is somewhat greater than in electrodialysis; however, since only one-half as many ion-selective membranes are used, the membrane cost savings can possibly compensate for the difference in power consumption.

PIEZODIALYSIS

Piezodialysis is a new membrane desalting process in the research stage using pressure as a driving force. It has intrinsic theoretical advantages compared to other desalting processes and appears to offer great promise. In contrast to reverse osmosis, which transmits potable water through a membrane, in piezodialysis a concentrated brine is driven through the membrane leaving behind the fresh product water. This means less material must be permeated through the membranes to produce potable water (since salt water is mostly water rather than salt), and one can achieve very high production rates with only modest permeation (flux) rates. Membrane imperfections or leaks only result in some of the feed water being rejected with the brine, rather than contaminating the product water.

The membrane used in piezodialysis is called a "charge-mosaic" membrane This is a single membrane made up of discrete cation-permeable and anion-permeable segments which are analogous to the two types of ion-selective membranes used in electrodialysis. Since these segments are in the same membrane, it is possible for both cations and anions to move through the membrane, i.e., concentrated salt is transported under pressure.

At the present time the process has been demonstrated on a bench scale unit which has operated very successfully. Further development is required, however, before the process can realize the full potential inherent in the intrinsic theoretical advantages which it possesess.

DISTILLATION

DISTILLATION IS ONE of the oldest ways known of separating fresh water from a salt-water solution. When salt water is boiled, the dissolved salt remains behind as the fresh-water vapor is boiled away. In a distillation process, the water is first boiled and then the steam, or water vapor, is cooled. This cooling condenses the steam into water again. See **figure 11.** Thus, distillation involves adding heat energy to salt water in order to vaporize the water and then removing the heat energy from the steam to condense it into fresh water.

Heat of Vaporization

When water is heated, its temperature increases until the boiling point is reached. While water is boiling, the steam and the boiling water are at the same temperature. However, raising water to its boiling point is not enough to cause it to boil. More heat must be added to change the water into steam. The amount of heat required to change liquid water into steam at the same temperature is called heat of vaporization of water. The heat of vaporization is of major importance in distillation. The amount of heat required to vaporize water into steam is approximately five times greater than the heat needed to raise water from its freezing point to its boiling point.

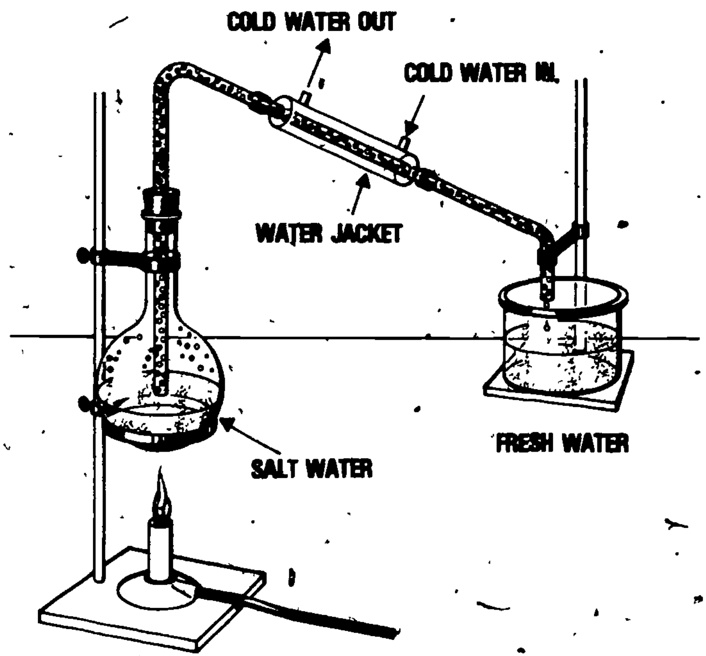


Figure 11

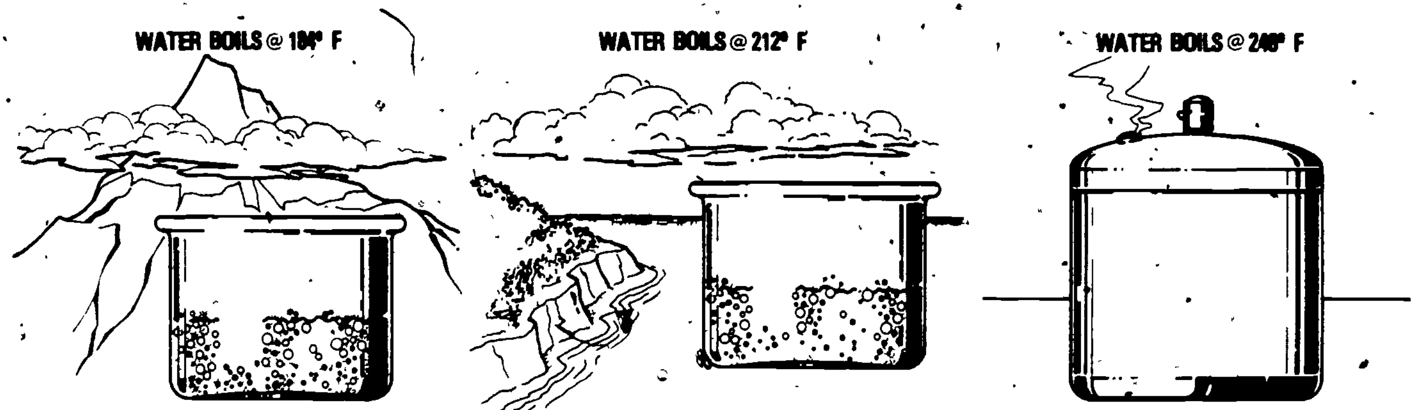
Boiling Point

At ordinary sea-level pressure (14.7 psi), water boils at 212° F. At low pressures, such as those that exist at high altitudes or that can be created in closed vacuum vessels, water boils at lower temperatures. The opposite is also true. At higher pressures, such as are developed in ordinary pressure cookers, the temperature must be raised above 212° F. before boiling will occur. See **figure 12**.

Heat Recovery and Scale Control

Because distillation is a two-step process involving both evaporation and condensation, heat must be added in one step and removed in the other. If these two steps were accomplished independently, the process would be inefficient and costly. In all the distillation processes discussed in the following pages, the steam is condensed by transferring heat from the steam to salt water as part of the heat source required to convert more water into steam. In this way some of the heat energy used in one step is recovered and used in the other step.

A common method of transferring heat from steam to the salt water is having the steam come in contact with metal tubes through which the cool incoming salt water is flowing. One of the major technological barriers faced by all distillation processes is preventing scale from forming on the heat-transfer surfaces Sea water is a very "hard" water due to the presence of calcium salts such as calcium sulfate. Unlike most other salts in sea water, which become more soluable at higher temperatures, calcium sulfate becomes less soluable as the temperature increases. When the solubility limit of a calcium salt is exceeded (at about 160° F.), a calcium scale begins to precipitate on the walls of the vessel or pipe in which the sea water is heated. This



MT. MCKINLEY PRESSURE = 50% OF SEA-LEVEL PRESSURE

SEA-LEVEL PRESSURE = 14.7 PSI

PRESSURE COOKER PRESSURE = TWICE SEA-LEVEL PRESSURE

Figure 12

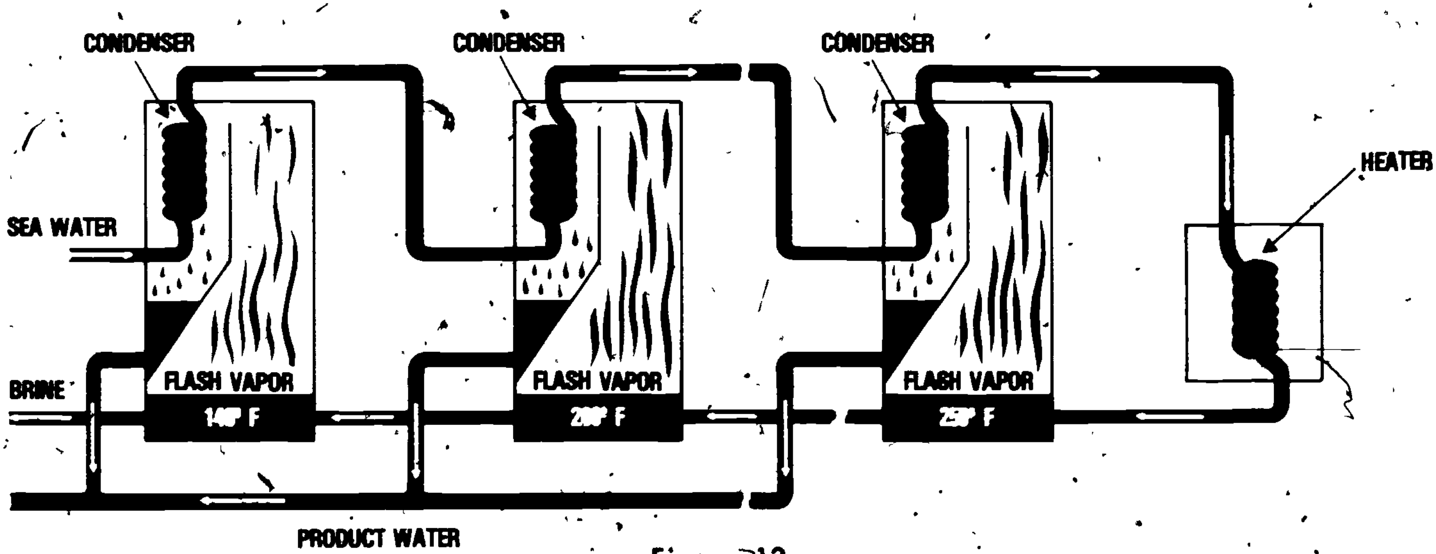


Figure 13

tenacious layer of scale acts as an unwanted insulator and decreases the flow of heat across the wall. Other substances in sea water may also contribute to the formation of scale.

By removing either calcium or carbon dioxide from sea water, it is presently possible to prevent calcium scale from forming at temperatures up to 250° F. Research has been undertaken to develop scale-control methods that will be effective at even higher temperatures. When these methods are fully developed the temperature of the salt water may be increased resulting in higher plant efficiency.

MULTISTAGE FLASH DISTILLATION

This process makes use of the fact that water boils at progressively lower temperatures as it is subjected to progressively lower pressures. The process which has received widespread commercial acceptance is illustrated in **figure 13.** The sea water is heated and then introduced into a chamber where the pressure is sufficiently low to cause some of the water to boil instantly, or "flash", into steam. Vaporization of some of the water results in lowering the temperature of the remaining brine. The brine then flows into the next chamber where the pressure is lower than in the previous chamber, more of the water flashes into steam, and the temperature is again reduced Condensation occurs when the steam comes into contact with the heat exchanger through which the incoming salt water flows before passing through the brine heater. In this way the heat that must be removed from the steam in order to condensate it into fresh water is transferred to the sea water, supplying it with some of the heat energy required to cause it to boil.

VERTICAL TUBE DISTILLATION

Figure 14 indicates how this process received its name. The salt water falls through a bundle of vertical tubes located inside a large chamber. As the salt water falls through the tubes, it is heated by steam that surrounds the tubes. This heat-exchange operation converts some of the water from the saline solution inside the tubes into steam and at the same time condenses some of the steam that surrounds the tubes into fresh water.

To obtain high efficiency in the recovery of heat energy, the process is repeated in several chambers which are arranged in series. The steam for the first chamber is supplied by a steam-generator plant, and the condensed water from the first chamber is returned to the steam-generator plant to be reconverted into steam. Steam generated inside the tubes of the first chamber flows to the second chamber where it surrounds the second bundle of tubes. The brine that did not vaporize in the first chamber is pumped to the top of the second chamber and flows downward through the second tube bundle. The steam that surrounds the tubes heats the brine as it falls, converting some of the water inside of the tubes into steam, and condensing some of the steam outside the tubes into fresh water.

This process is repeated through several chambers until most of the heat energy supplied in the first chamber is recovered. The temperature of the saline water drops as it progresses through the series of chambers. In an experimental plant at Freeport, Tex., the salt water entered the first chamber at 250° F and entered the twelfth, and last, chamber at approximately 90° F. The pressure in each chamber was also progressively reduced to permit vaporization to occur at lower temperatures. The brine that collected at the bottom of the last chamber was returned to the sea.

Each separate chamber in which distillation occurs is called an "effect". Thus, this process is sometimes called the "vertical tube, multiple-effect distillation process".

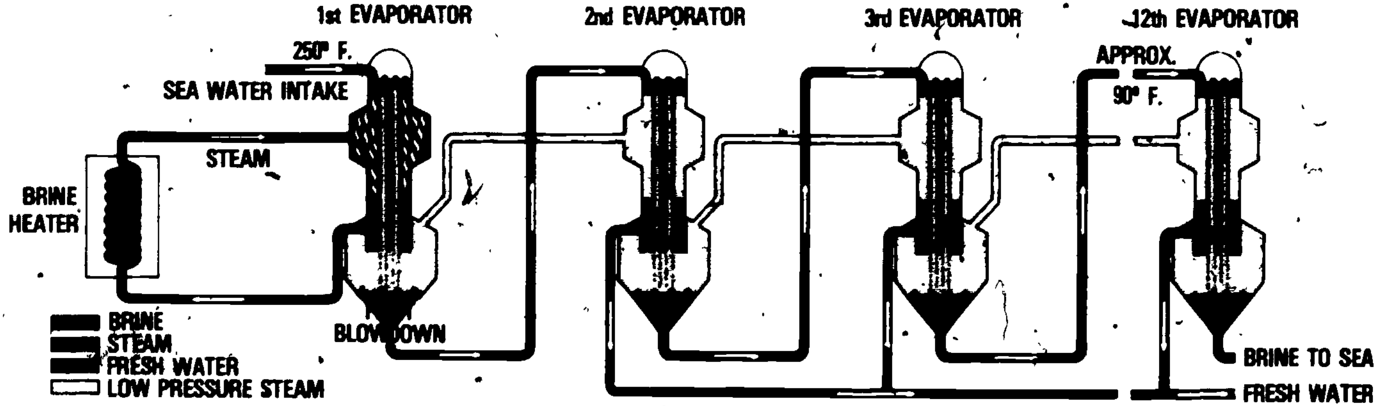


Figure 14

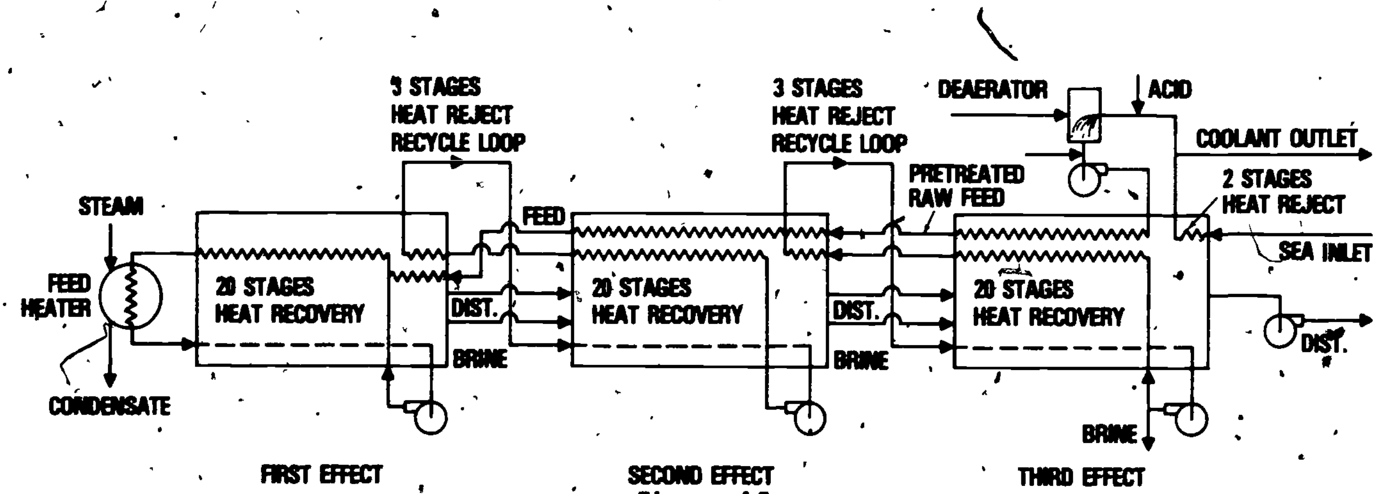


Figure 15

MULTIEFFECT MULTISTAGE DISTILLATION

The multistage flash process discussed previously is also designated "SEMS" for single-effect multistage". The multieffect multistage (MEMS) process is an advancement over the SEMS process. Up to a point, the flash process becomes more efficient as the number of stages used for vaporizing and preheating increases. The available pressure difference needed to move the brine from chamber to chamber at the low-temperature, low-pressure end of the cycle is the limiting factor in the quantity of water circulated and the number of stages that can be employed in a SEMS plant. The temperature changes are usually limited to about 4° F. per stage because of the low pressure differential available at the high vacuum conditions that exist in the final few stages. The MEMS process makes it possible to add more stages for each temperature interval as pressure differences increase by breaking up the conventional single circulating path into a number of circulating loops. The increasing circulation rates in the higher temperature effects, combined with more stages in a given temperature interval, provide greater economy.

Separating the process into a number of effects, each operating at a different temperature, permits better control of scale. A multiple-effect unit separates the recirculation of brine and produces low brine concentration in the high-temperature effects.

A diagram of the MEMS process is shown in **figure 15.** The salt water is preheated in two stages and is then treated with acid to prevent the precipitation of scale from the feed salt water. Preheating continues through a number of stages until the first effect is reached. From the first effect, some of the brine is recirculated through the brine heater, and some is passed to the second effect. The partial recirculation and partial progression to succeeding stages continues until the final effect, where the highly concentrated brine is either discharged or passed to a byproduct-recovery unit.

VAPOR COMPRESSION DISTILLATION

When a vapor is compressed, its temperature and pressure increase and its volume decreases.

In each effect, brine is pumped upward through a tube bundle into a large spherical chamber. As the brine travels upward, it is heated by the steam that surrounds the tubes. This transfer of heat causes some of the water to vaporize after it leaves the tubes A mixture of vapor and brine enters the spherical chamber. Some of the brine is returned to the bottom of the tube bundle and recirculated, some of the brine is discharged The vapor from the second effect, which is on the right in **figure 16**, is drawn off by the compressor and the higher temperature vapor that leaves the compressor is transferred to the first effect. The vapor discharged from the compressor surrounds the tube bundle in the first effect, and supplies heat to the brine that is traveling upward in the tubes. The vapor that forms in the spherical chamber in the first effect is transferred to the second effect where it supplies heat to the brine that is being pumped through the second-effect tube bundle. As the vapor in both effects loses heat to the brine. some of the vapor condenses. The condensate falls to the bottom of the effects and is pumped off as product water.

The primary difference between this process and other distillation processes is in the method by which heat is added to the system In other processes, saline water is heated with steam in order to cause some of it to boil. In this process, however, heat is added to the vapor by converting mechanical work into heat of compression.

Most of the energy is consumed by the motor that drives the compressor. Steam heat is added directly only during startup

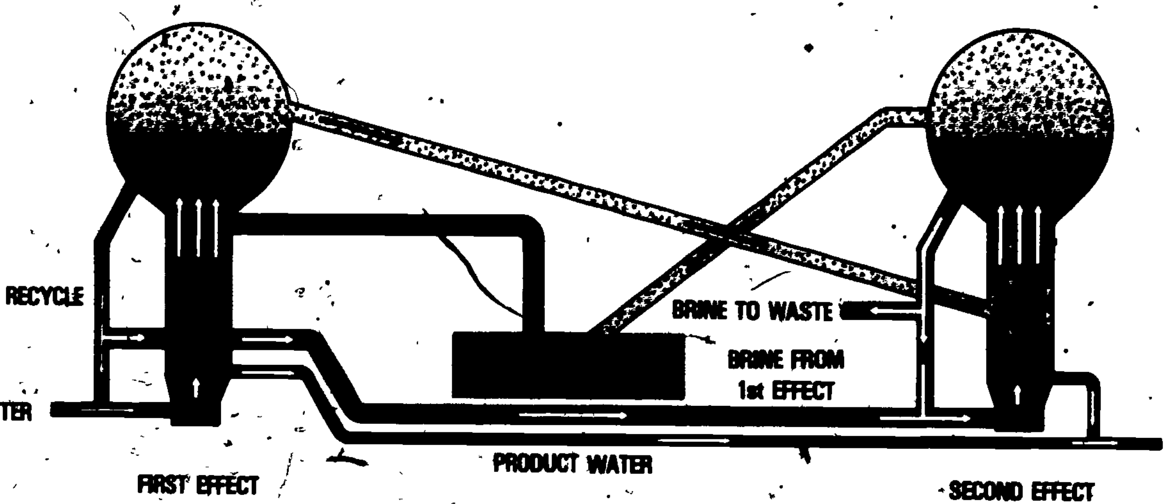


Figure 16

Preconditioning

In addition to the main processing equipment, auxiliary equipment is used to treat incoming salt water before it enters the evaporators. In the auxiliary processing steps, chemicals are mixed with the salt water to prevent formation of scale on the heat-transfer surfaces. The salt water also passes through heat exchanger before it enters the tubes. The brine that is being discharged and the product water are used to preheat the incoming salt water. By preheating in this manner, the salt water is raised almost to the boiling temperature before it reaches the evaporator, and the product water leaves the system at a temperature that is only about 15° F. above the temperature of the incoming salt water.

SOLAR HUMIDIFICATION

The solar-humidification process makes use of the fact that water will evaporate from a free surface, even though the water is at a temperature below its boiling point. The rate of evaporation of the water depends largely on two factors: the temperature of the water and the relative humidity in the space above the free surface of the water. The conversion process takes place in an apparatus called a solar still. The operation of a solar still is illustrated in **figure 17.** A solar still utilizes the same principles that keep a greenhouse warm on winter days. The sun's rays pass through the glass top without giving up any significant amount of energy. The sun's energy is absorbed by the black surface on the bottom of the still. The temperature of the water in contact with the heated black surface increases, and the water evaporates.

Because the glass top of the solar still is not heated by

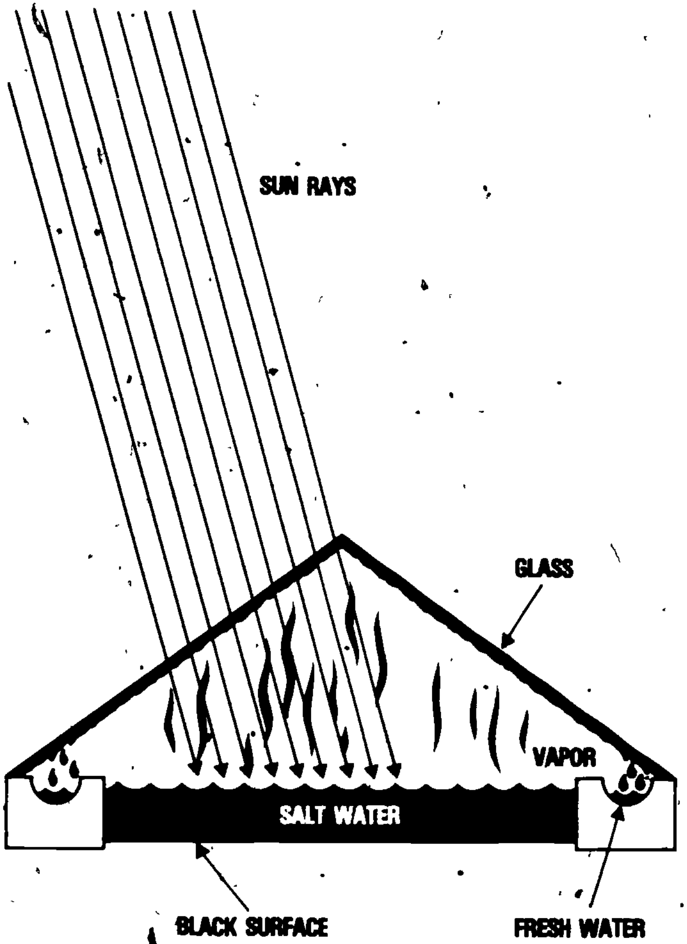


Figure 17

the sun's rays as much as the black surface, the temperature of the top remains lower than that of the vapor. Because of this temperature difference, the water vapor that comes in contact with the top condenses and runs down into the collecting trough. As some of the vapor is removed from the space above the water surface by condensation, the relative humidity decreases, tending to increase the rate of evaporation.

Conversion rate

The obvious advantage of this process is that the energy required for conversion is free. Furthermore, labor and maintenance are minimal. However, the disadvantages are equally obvious. The conversion rate depends on the intensity of the sun's rays, which varies according to geographical location, time of year, and the extent of cloudiness, fog, or haze. Even under ideal solar-transmission conditions, only about 1 pint of fresh water can be obtained each day for each square foot of surface that absorbs the solar energy.

The evaporation rate depends on the depth of the water being heated by the absorbing surface. Because the rate of evaporation depends also on relative humidity, the conversion rate is highest when the temperature of the glass top is lowest, because at low temperature condensation occurs more rapidly.

Even though the conversion energy is free, efficiency is an important factor in solar humidification because of the relationship between surface area and conversion quantity.

When solar energy contacts any surface, the energy divides in three ways. Some of the energy is absorbed by the surface, some is reflected away, and some is transmitted through the surface. Black surfaces absorb the most energy, white or polished metal surfaces reflect the most energy, and transparent surfaces transmit the most energy. Thus, selection of materials is important not only from a cost of materials standpoint but also from a standpoint of utilization of solar energy, which determines the efficiency of surface utilization. Insulation is often used to reduce heat losses into the ground. For shallow basin stills, which operate at relatively high temperatures, insulation is an important consideration in obtaining economic advantages. All joints must be carefully sealed to prevent escape of the heated vapor.

CRYSTALLIZATION

IT IS WELL KNOWN THAT a salt solution cooled to its freezing temperature will deposit ice crystals of pure water. This principle forms the basis for desalting water by the freezing process.

Heat of Fusion

When a pound of ice melts, it absorbs 144 Btu of energy, called the latent heat of fusion, without any change in temperature. This heat of fusion equals exactly the quantity of heat that was removed in producing the ice originally. In other words, the latent heat of fusion equals the latent heat of crystallization. In the first instance, a certain quantity of heat is absorbed by the ice in converting the ice into water; in the latter instance, an equal quantity of heat is removed from the water in converting the water into ice.

Advantages of the Freezing Process

The application of freezing to the desalting of sea water involves three major steps: viz, partial freezing of the feed stream to an ice-brine slurry, separation of the ice crystals from the brine, and melting of the ice. The freezing process has the following theoretical advantages: First of all, it has the smallest energy requirement of any process which involves a phase-change. See **figure 18.** In addition, there is a minimum of corrosion and scaling because of the low temperatures involved. This latter advantage also makes possible the use of lower-cost construction materials and equipment as a means of reducing capital investment.

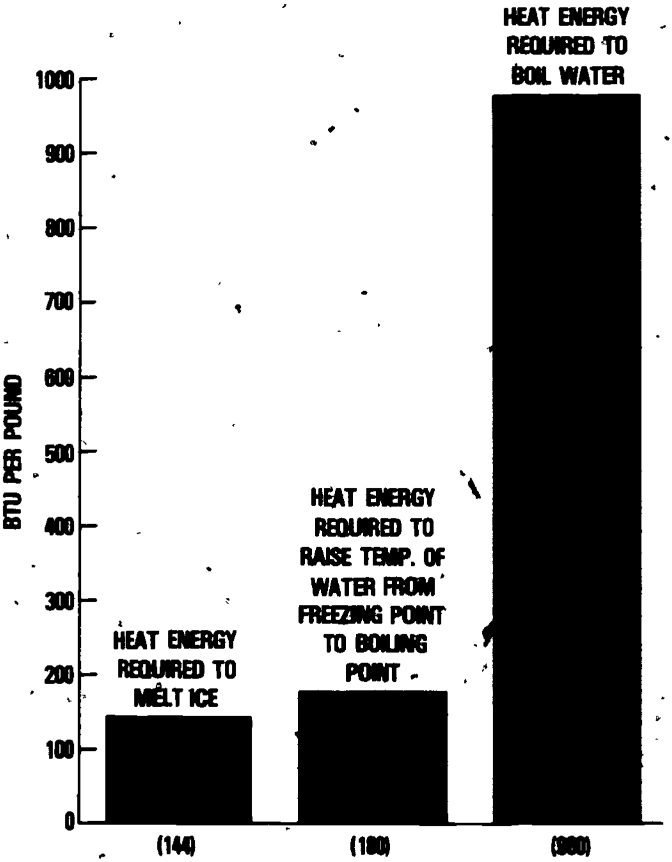


Figure 18

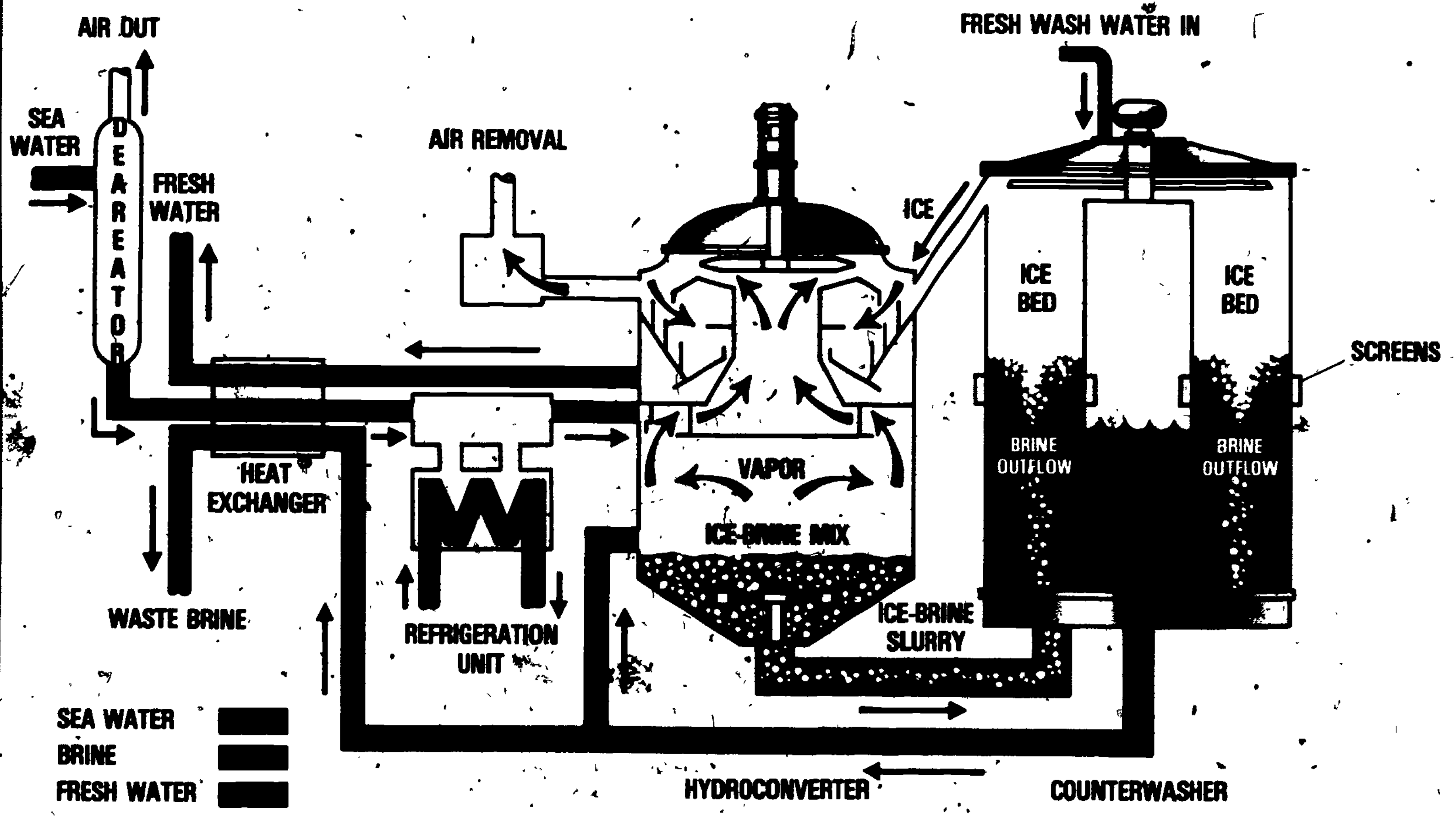

AIR OUT
SEA WATER
DEAREATOR
FRESH WATER
AIR REMOVAL
FRESH WASH WATER IN
ICE
ICE BED
ICE BED
SCREENS
BRINE OUTFLOW
BRINE OUTFLOW
VAPOR
ICE-BRINE MIX
ICE-BRINE SLURRY
HEAT EXCHANGER
WASTE BRINE
REFRIGERATION UNIT
SEA WATER
BRINE
FRESH WATER
HYDROCONVERTER
COUNTERWASHER

Figure 19

To preserve the inherent economic advantages of freezing, direct contact methods of refrigeration are employed; the need for expensive heat-transfer surfaces for heat removal, or recovery is therefore avoided.

Variations of the Freezing Process

Freezing may be accomplished by the flash evaporation of sea water at a low pressure (3 mm Hg) or by vaporizing a refrigerant such as butane in direct contact with the sea water. The process variations are described in the following sections.

VACUUM FREEZING-VAPOR COMPRESSION

In the vacuum freezing-vapor compression process, the latent heat of fusion is given up when precooled sea water is introduced into a chamber at a very low pressure. An advantage of the process is that no cooling medium or heat-transfer surfaces are used to accomplish freezing. The process is illustrated in **figure 19.** The sea water is passed through a dearator to remove air and noncondensable gases. The deaerated water is then cooled by heat exchange with the product-water and waste-brine streams. This cold, deaerated sea water is then introduced into the lower section of the chamber, known as the hydroconverter, which is maintained at a low pressure (3 mm Hg). This low pressure causes a portion of the water to vaporize, thus removing heat from the sea water. Approximately one-half of the sea water is frozen into ice crystals.

The mixture of ice crystals and brine, called a slurry, is pumped to the bottom of a separation column, or counterwasher. The slurry rises within the column and the ice crystals are compacted to form a porous bed of ice. The bed is moved upward by a slight positive pressure caused by the brine flowing through the bed and outward through screens positioned approximately at the middle of the column. The rising ice bed is washed countercurrently with less than 5 percent of the total fresh water product of the plant. The ice is then removed by means of a mechanical scraper at the top of the column, and the scrapings are dumped into the melter, or upper section of the hydroconverter.

When sea water enters the lower section of the hydroconverter, some of the water flashes to a vapor. This vapor is then compressed by a specially designed compressor located at the top of the hydroconverter. The compressed vopor is then condensed on the washed ice entering the melter, or upper section of the hydroconverter. Because the compressed vapor contains the heat originally removed from the sea water in the freezer, the ice is melted to fresh water. Waste brine from the wash column and product water from the melter are discharged from the process, one to waste disposal and the other to the consumer.

SECONDARY REFRIGERANT FREEZING

The secondary-refrigerant freezing process differs from the vacuum-freezing process principally in the method by which freezing is accomplished. In the former method a refrigerant, such as butane, is evaporated in direct contact with the sea water to remove the latent heat of crystallization (144 Btu/lb) in order to partially freeze the sea water.

The process is illustrated in **figure 20.** Sea water is precooled by heat exchange with the product-water and waste-brine streams. The sea water enters the freezer where liquid butane is bubbled through the sea water. The butane vaporizes and lowers the water temperature. This results in the formation of salt-free ice crystals in a more concentrated sea water or brine. Approximately one-half of the sea water is frozen into ice crystals. The ice-brine slurry is then pumped to a washer-melter. The slurry rises within the washer and the ice crystals are compacted into a porous bed of ice. The bed of ice is moved upward by a slight positive pressure caused by the brine flowing through the bed and outward through screens positioned near the middle of the column. The rising ice bed is washed with less than 5 percent of the total product water. The ice is then removed by means of a mechanical scraper into the outer annulus; that is, the melter. The butane vapor, which contains the heat removed to form the ice, is compressed in the primary compressor and then introduced into the melter where it condenses on the ice. Heat is given up and the ice is melted. The condensed butane and the product water flow together to a decanting unit where the two liquids are separated.

From the decanter, the product water leaves the process and the liquid butane is recycled back to the freezer. Butane vapor not required for ice melting is further compressed by the secondary compressor and then condensed in the butane condenser, which is cooled by sea water. The liquid butane is recycled to the freezer.

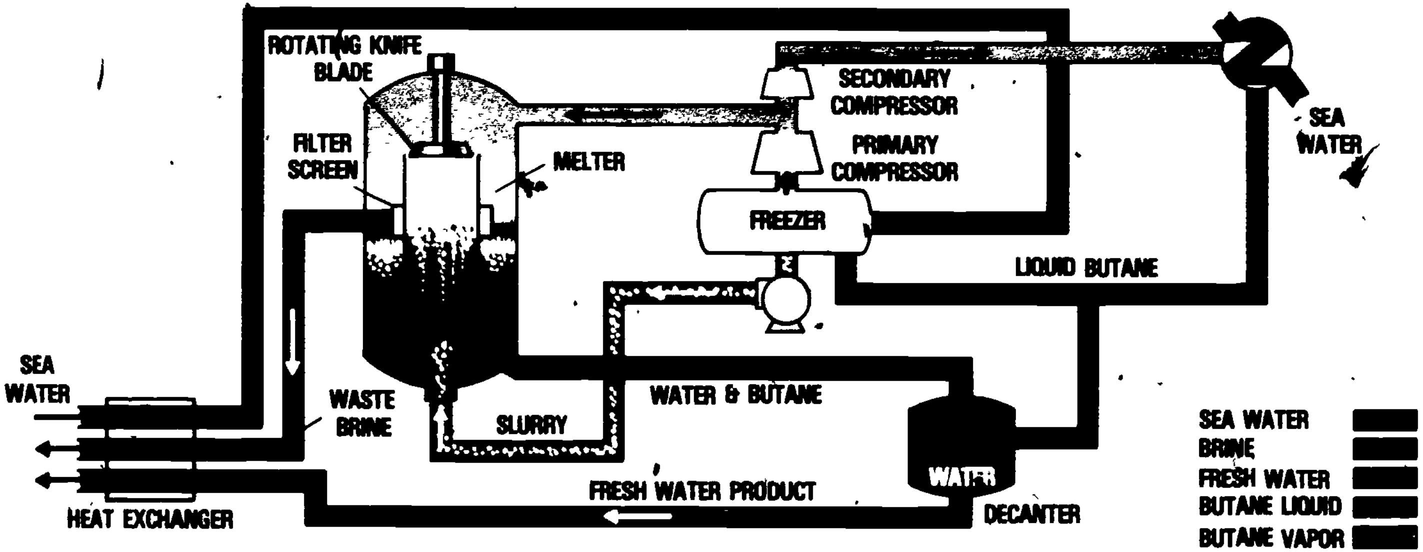


Figure 20

EUTECTIC FREEZING

When the freezing process is operated to increase the brine concentration in the freezer, a point is eventually reached where both ice crystals and salt crystals are formed simultaneously. At that point the concentration of dissolved solids and therefore the freezing point of the solution remain constant. Operation of a freeze desalting process under these conditions has been termed "eutectic freezing". Using sodium chloride as an example, the eutectic freezing point would be −6° F. at a constant concentration of 23.3 percent dissolved solids.

It has been found to be technically feasible to continuously separate ice and salt crystals individually from the brine thereby reducing the effluent streams from the desalting plant to fresh water and wet salt. The secondary refrigerant type process would normally be used for eutectic freezing with at least two stages of freezing to reduce power consumption. The low temperature eutectic stage freezer would require a more powerful refrigerant compressor because of the large temperature difference between the freezer (−6° F.) and the melter (32° F.). The bulk of the fresh water product would therefore be produced from a first stage freezer operating at a lower brine concentration and correspondingly higher freezing temperature.

HYDRATE FORMATION

The hydrate process is based on the formation of a crystalline substance by the combination of low-molecular-weight hydrocarbons or their derivatives with water. The resulting crystalline compounds are known generally as solid clathrate substances. Specifically, a clathrate is an inclusion complex in which the molecules of one substance are contained or enclosed within the crystal lattice of another component. Like ice crystals, clathrate hydrates reject salt ions and water molecules enclose a guest, hydrocarbon, within their lattice (**Fig. 21**).

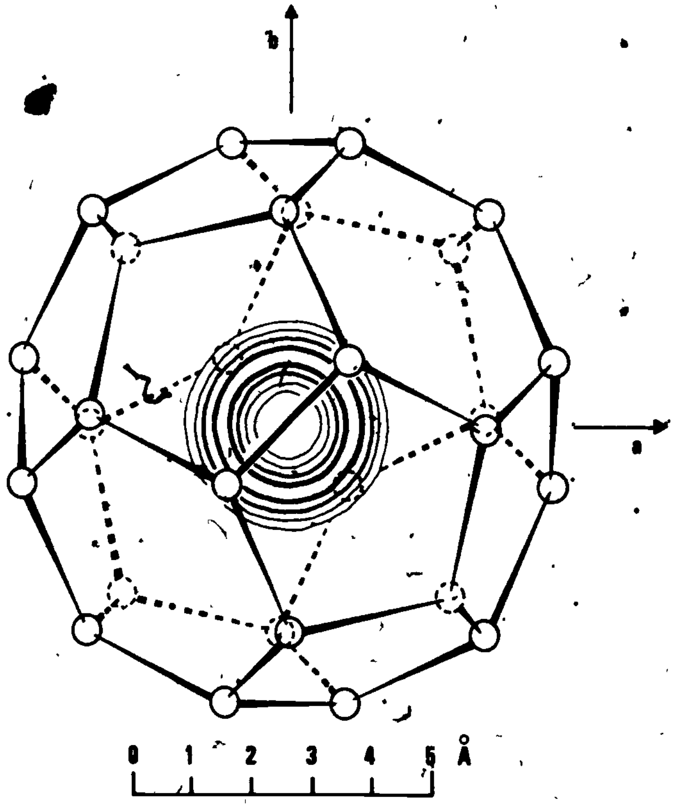


Figure 21

In the hydrate process, sea water and a hydrating agent such as propane are brought into intimate contact in a crystallizer. When the temperature and pressure are adjusted to proper levels, hydrate crystals form. The crystals are separated from the brine and then washed with a small portion of fresh water. This step is accomplished in a vessel known as a wash-separator. The crystals in slurry form are pumped to the melter-condenser where they are decomposed by melting. The latter step is accomplished by condensing compressed propane vapor on the crystals, thus providing the necessary heat to melt the crystals. Because propane is insoluable in water, two immiscible liquids (water and propane) result when the hydrate crystals are melted. The two liquids have different densities and therefore may be separated in much the same way that water and oil are separated, viz, by decantation. The two liquids are collected in the decanting vessel, the propane separating out and floating on top of the water layer. The water is drawn off into a suitable storage container, and the liquid propane is pumped back to the crystallizer to continue the process of hydrate formation. As is evident, the operational steps involved in the hydrate process are basically the same as those used in the secondary-refrigerant freezing process. Therefore, an individual flow diagram has not been included for the hydrate process.

An ideal hydrating agent would be nontoxic, nonflammable, available in large quantities at low cost, and would not impart an objectionable taste to the product water. Fundamentally, it is also desirable that the crystals have a low heat of fusion so that decomposition may be accomplished with relatively little energy exchange.

CHEMICAL PROCESSES

SALINE WATER MAY BE SEPARATED into pure water and salt or concentrated brine by chemical methods. Either the salts or the water may be made to undergo a chemical reaction to form a substance that is readily separated.

In the ion-exchange process the salts react with specially formulated resins that are reactive but insoluble. One kind of resin takes up sodium ions and other cations and releases hydrogen ions. A second type of resin takes up chloride ions and other anions and releases hydroxyl ions. The hydrogen ions and hydroxyl ions combine to form small amounts of water. The original saline water is deionized, that is, it is freed of dissolved salts.

ION EXCHANGE

An ion exchanger is a porous bed of certain resin materials that have the ability to exchange ions held in the resin with those in a solution that contacts the bed. Minerals and resins are available which exchange ions with either cations or anions. In the former case, the process is called cation exchange, and in the latter case, anion exchange. When a solution containing cations is passed through a cation exchanger, the cations from the solution are exchanged with cations from the bed material. The cations from the incoming solutions remain bound to the exchanger, and those from the bed material leave with the outgoing solution. A similar exchange of anions occurs in flow through an anion exchanger.

Numerous substances of both natural and synthetic origin possess ion-exchanging properties. The materials of interest in saline water conversion are synthetic resins. The synthetic resins are plastics chemically prepared for specific ion-exchange properties.

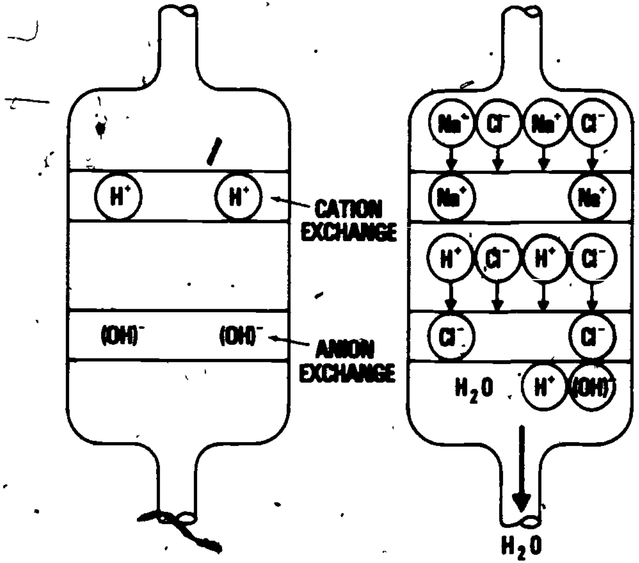


Figure 22

In the ion-exchange conversion process, both cation and anion exchangers are used. The ion-exchange beds are usually placed in series, although mixed feeds may be used, and the saline solution passes first through the cation exchanger and then through the anion exchanger. An example of the ion-exchange process is illustrated in **figure 22.** The cation exchanger is an acidic resin that exchanges its hydrogen ions for the sodium ions in the incoming solution. The anion exchanger is a basic resin that exchanges its OH^- ions for the chloride ions in the solution. The OH^- ion is called the hydroxide ion. In the arrangement shown in **figure 16,** a saline solution containing sodium and chloride ions enters at the top of the conversion unit.

When the solution contacts the cation exchanger, the sodium ions are exchanged for the hydrogen ion, and the chloride ions pass through unaffected. Thus, the sodium chloride solution is converted into a solution of hydrogen and chloride ions, which is actually a dilute solution of hydrochloric acid. As the acid solution flows through the anion exchanger the chloride ions are exchanged for hydroxide ions When the hydroxide ions are released, they combine with the hydrogen ions, forming molecules of pure water.

As the conversion process continues, the resins are progressively saturated until finally they lose their ability to remove sodium or chloride ions. When this point is reached, the conversion process must be halted while the resins are regenerated. Regeneration is accomplished by washing the resin beds with acids or bases that restore the original ion-exchange properties to the exchangers.

Regeneration costs have limited ion exchange to applications where salts are in low concentrations, less than 2–3000 mg l. The process can be used to obtain small amounts of fresh water from sea water in cases where energy sources are not available. Emergency kits for liferafts are one example of this application.

SALINE WATER CONVERSION PLANTS

TEST PROGRAMS have been conducted for each of the saline-water conversion processes discussed above. Some of the processes have been tested on a laboratory scale, and some have advanced to the test-bed-plant stage. The objective of the testing has been to obtain information on the chemical and physical feasibility of various processes. The objective of the test-bed-plant operations has been to obtain and confirm information on equipment design and operating procedures for application to large-scale conversion plants.

Experience to date indicates that there is a need for a number of conversion processes. Factors such as type and quantity of available energy, production capacity required, and concentration of feed water all combine to determine which process is the most suitable and economical for a given geographical location.

Dual-Purpose Plants

Combining saline water conversion with electric-power generation shows promise as an economical method of producing large quantities of fresh water. In a dual-purpose plant the heat energy that remains in the steam after it passes through a steam turbine is used as the heat source for a distillation conversion process. High-temperature, high-pressure steam is used to power a turbine that drives an electric generator. The turbine exhaust steam is fed to a saline-water conversion plant where it condenses as it gives up more of its heat energy, and the condensate is then returned to the steam generator.

Tripurpose Plants

When the capacity of the saline water conversion unit is relatively high, a third function, byproduct recovery, may be incorporated in the plant with improved overall economy. In a tripurpose plant, the brine is routed to a byproduct-recovery unit where minerals of significant concentrations with commercial value are extracted. The three minerals of greatest economic potential in sea water (excluding fresh water) are salt, magnesia, and potash. One sea water desalination plant producing 50 million gallons per day of fresh water and operating at a brine concentration factor of 3:1 could also produce about 20 percent of the U.S. annual salt requirements, 25 percent of the magnesia, and 1 percent of the potash. More salt and magnesia could be produced than utilized at a given location; however, this is not true for potash. The plant could produce 150 tons per day of potash (K_2O) which would have a value of $6,000–$10,000 depending on whether it was recovered as the chloride or sulfate.

DESALTING APPLICATIONS

DESALTING PLANTS INVENTORY REPORT NO. 5*, prepared for the Office of Water Research and Technology by the National Water Supply Improvement Association. provides the following data for land based desalting plants in operation or under construction of 25,000 gallons per day or larger as of January 1, 1975.

REGION	NUMBER OF PLANTS	PLANT CAPACITY MILLION GALLONS PER DAY
United States and territories	372	88
North America (except U.S.	41	12
South America & Caribbean	63	38
Europe	218	84
Africa	104	57
Arabian Peninsula & Iran	153	146
Asia & Indonesia	68	68
Australia and [illegible] Pacific	10	2
Union of Soviet Socialist Republics	7	30
	1036	525

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* This publication may be purchased through NTIS, Springfield, Virginia Order number PB [illegible]43556

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GLOSSARY

Anion—a negatively charged ion.

Brackish water—water ranging from 1,000 to 35,000 parts per million of total dissolved solids.

Brine—any concentrated water solution containing dissolved salts.

Cation—a positively charged ion.

Corrosion—a chemical attack on a metallic surface, often causing a structural weakening of the metal.

Effect—A process such as distillation may be performed at one temperature and pressure or it may be performed in a series of steps at graduated temperatures. Each complete step in such a process is called an effect.

Fresh water—water containing less than 500 parts of dissolved salts per million parts of water. Water containing more than 1000 parts of dissolved salts per million parts of water should not be used for human consumption.

Heat of fusion—the amount of heat which must be added to unit mass of a solid substance as its melting point to convert the substance into liquid at the same temperature and pressure.

Heat of vaporization—the amount of heat which must be added to a liquid at its boiling point in order to convert the substance into vapor at the same temperature and pressure.

Hydrate—a crystallized substance formed by the association of water molecules with certain chemical compounds.

Ion—an electrically charged atom or group of atoms.

Membrane—a thin sheet of plastic or other material. If it has the ability to permit certain substances to pass through it and exclude others, it is called a semipermeable membrane.

Osmosis—the diffusion through a semipermeable membrane separating two solutions which tends to equalize the concentration of the solutions.

Saline water—brackish water, sea water, or brine, containing more than 1,000 ppm of total dissolved solids.

Scale—a hard incrustation that forms inside a vessel in which water is heated. Scale is objectionable because it reduces heat transfer.

Stage—a part of a process which is being undertaken in progressive similar steps.