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DESALINATION PROCESSES

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INTRODUCTION

The variety of desalination methods available today were all devised based on prior observation of natural salt-water separation processes. Thus, we have techniques that imitate the process of sun heated sea water evaporation, followed by rain cloud formation that eventually replenishes rivers, lakes and wells, and others based on natural seawater freezing. The ice formed on both poles is salt-free, with the salt remaining in the surrounding waters. Still another man-made desalination process was devised after observation of plant life's absorption of the earth's waters, and of how the cells of the human body absorb and eliminate toxins, which led to desalination processes using semi-permeable membranes. Thus, observation of these elementary principles of nature is the prime source of inspiration underlying the desalination techniques we use today. The differences that have since arisen in commercial processes are due to efforts to determine the most effective, cost-efficient way of separating the two in man-made facilities.

The following is a non-exhaustive past and present list of noteworthy processes:

DISTILLATION PROCESSES

• Submerged Tube Evaporation (S.T.)

• Multi-stage Vertical Tube Evaporation (V.T.E.)

• Multi-stage Flash Evaporation (M.S.F.)

• Horizontal Tube Multi-effect Evaporation (H.M.E.)

• Mechanical Vapor Compression (M.V.C.)

• Thermal Vapor Compression (T.V.C.)

• Solar Distillation (S.D.)

MEMBRANE BASED SEPARATION PROCESSES

• Reverse osmosis (R.O.)

• Electro-dialysis (E.D.)

• Nanofiltration (U.F.)

FREEZING

• Freezing (FREEZ)

The processes most frequently used in commercial operations in Spain and worldwide are described in detail below.

Three of the methods listed above are will not be described: Freezing, which never got beyond the pilot stage, and S.T. and V.T.E., two early methods used mainly on ships, which have since become obsolete.

Distillation Processes can be used to desalinate both seawater and brackish water, but in practice are used exclusively on seawater. Reverse Osmosis Membrane Separation is used on both seawater and brackish water, while Electrodialysis and Nanofiltration are used exclusively on brackish water.

PRINCIPAL DESALINATION BY DISTILLATION PROCESSES

Multi-stage flash evaporation (MSF)

The idea of this process is to distill seawater and condense the steam obtained, thus recovering latent heat to heat more seawater that will later evaporate. If the heat transmission took place over an infinite area and infinite number of stages, with no heat loss along the way, once the process began, no further heat would be needed, and the process would be self-sustaining. But, since this is thermodynamically impossible, an outside energy source is required to supply the higher temperature required to initiate the cycle.

Using the flow diagram in *Figure 1*, we will describe how the process works. The three sections shown are: Heat Rejection, Heat Recovery and Reheater. Our explanation starts at the point of brine output from the reheater. Here, the make-up water is at maximum admissible cycle temperature, and circulates into the first evaporator stage from the bottom up. In this stage, the brine is pumped into a chamber kept at temperatures slightly below the make-up water´s vapor saturation pressure, due to which part of its water content flashes into steam to achieve equilibrium and adjust its temperature to the pressure of that stage. The flash steam then passes through demisters, where it is stripped of any suspended droplets adhering to the vapor during flashing. The vapor condenses on the outer pipe surface, and drips down into a collection tray.

The unflashed brine then enters a second stage, where it flashes to steam at a lower pressure. The flash-cooling process is then repeated stage by stage to the last stage where the heat rejection section is carrying seawater intake. The heat rejection stage issues heated up seawater. The part of it returned to the sea is known as blowdown brine, and the other part, which rejoins the cycle after degassing and chemical treatment to prevent corrosion and scaling, is known as product water.

Product water is then mixed with partially flashed brine from the previous stage to constitute make-up water. This cooler combination is then pumped into the pipes of the heat recovery section to condense the steam formed during each stage. Recovery or make-up water gradually heats up as it progresses up to stage one. After this stage, its temperature will be close to that required for cycle initiation. The steam condensate from the reheater will provide the boost required to bring it up to maximum temperature.

The reheater condensate is then flushed back into the steam production cycle.

Product water from each stage is then circulated through a series of hydraulic chambers, into the following stage. It adjusts to stage pressures through partial flash, followed once again by condensation on the pipes. By the time it reaches the last stage of the evaporator, the product temperature has cooled, and released all sensitive heat. The product is then pumped out of the collection tray and sent to the storage tank.

Because seawater is being constantly pumped into the evaporator, the same amount of salt must be extracted to maintain a proper saline balance and avoid salt accumulation and concentration. For this, a brine purge is done during the last stage, at the point of maximum salt concentration.

Because seawater air and gas content is not fully eliminated during pretreatment, and also because many of the stages take place in a vacuum, air usually seeps in through pores, pipe flanges and other equipment. These incondensable gases must be extracted from the evaporator to avoid accumulation that would lower performance, so vacuum and venting systems are installed in the stages. This equipment is normally comprised of ejectors with barometric or surface condensers.

Horizontal tube multi-effect evaporation (HTME)

The idea of this process, as with all distillation, is to evaporate seawater, condense the steam obtained, and recover latent heat to heat more seawater for subsequent evaporation.

Using *Figure 2*, we will describe how the process works. The evaporator is divided into two sections: the condenser, which is the coolest point of the evaporator, and the effects, with the first effect being the hot point of the thermal cycle. We will start from this first effect. The steam used, normally as a low level energy source, condenses inside the tubes while the outside of the tubes is being sprayed with a colder seawater, which is heated up to maximum temperature and partially evaporates.

The steam produced in this first effect filters through demisters to eliminate any remaining brine, and enters the tubes of the following effect where it condenses, while part of the seawater being sprayed on the outside of the tubes also evaporates. The unevaporated sprayed seawater from the first effect is called feedwater. Due to the lower pressure encountered in the subsequent effect, and also to the heat from the condensation occurring inside the tubes, the feedwater flashes the same quantity of water into steam. In other words, steam is produced in each effect due to the thermal imbalance encountered from effect to effect, and to condensation occurring inside the tubes. The process is repeated, effect after effect, each at a lower temperature and lower inside pressure, down to the last effect, at the condenser.

This condenser is the cool end of the cycle where the vapor produced by the previous effect is condensed. In this last effect, no steam is produced, because the abundance of seawater used keeps temperatures below those required for steam production. After this effect, the flow of hot seawater is channeled two ways: reject water, which is returned to the sea, and feedwater which is pumped back into the effects, in ascending order, (from next to last to first effect). The feedwater is sent to the heat exchangers of each of the effects, which use part of the steam produced to heat it as it moves up to the first effect, where it reaches the maximum temperature required to continue the cycle. As noted earlier, in this initial effect, the temperature of the feedwater rises and it partially evaporates when sprayed on the tubes. The unevaporated seawater remaining in this effect is then pumped into the following effects where it is used for further tube spraying.

The highest salt concentrations form in the last effect prior to the condenser from the seawater that has partially evapo-

rated in previous chambers. This is where the brine purge is needed to maintain evaporator saline balance.

The steam condensed in the first effect is returned to the external cycle. The condensate from the second and following effects is the product, which is circulated through the effects at increasingly lower pressures, due to which part of the product water evaporates in an effort to balance pressures and temperatures. This steam is mixed with the rest of the steam produced in the effect which, in turn, condenses in the following effect. Thus, when the product flow reaches the condenser, it is at the lowest possible temperature. From there, a product pump sends it to the plant storage tank.

Because the seawater releases gases during the evaporation process, and the evaporator works in a vacuum, leaks occur and air seeps in through pores and other points. If allowed to accumulate inside, the air affects heat transfer and lowers performance. To avoid this, each effect has a venting system, and a vacuum pump to extract non-condensable gases.

Before the feedwater is sent to the evaporator, it undergoes chemical treatment to prevent scaling, usually a combination of degasification and inhibitors.

Mechanical and thermal steam compression

The diagram in *Figure 3* will help us explain this process. This type of plant has three main sections: A compressor or ejector; a single or several stage evaporator; and a liquid/liquid heat exchanger.

The salt water intake is sent to the heat exchanger for heating. The seawater is then fed into the cycle, and mixed with part of the brine to constitute the feedwater which is then pumped into the evaporator. A series of nozzles then spray it on the condenser tubes. The feedwater is heated to the saturation point for the pressure inside the evaporator, and partially evaporates as it continues to absorb heat. The vapor formed then passes through demisters, and is drawn into the compressor, where it is further compressed to become a superheated vapor. This vapor is circulated through the evaporator tubes where it first loses its sensitive heat, and then condenses, sending remnant heat to the feedwater being

sprayed on the outside of the tubes. A product pump extracts the product, which still carries some sensitive heat, to the heat exchange plate where it heats the seawater being pumped into the cycle.

The unevaporated input falls to the bottom of the evaporator where it is pumped out along two different routes: one is combined with the intake seawater to become feedwater, and the other is used for the brine purge required to maintain saline balance. Because the purge retains some sensitive heat, it is cooled in the heat exchange plate, and the heat recovered goes to the seawater that is being sent to the evaporator.

Before the seawater is sent to the degassing cycle, it undergoes chemical treatment to prevent scaling and corrosion. A vacuum pump extracts incondensables from the evaporator.

The above is the process used for Mechanical Steam Compression. If an ejector serving as an outside steam source is used instead of a compressor, the process is called Steam Ejector Compression. The most important difference is that in Steam Ejection, the ejected steam is combined with that of the external steam source and steam produced inside the chamber, and the product obtained must therefore be branched into two flows: one with the same weight as the impelling steam, which is sent back to the boiler that produced it, and another, which is the product.

Solar Distillation

Figure 4.2 depicts a simplified example of a solar distillation module. It consists of a low closed off pool with a transparent glass roof and two layers of flooring: heat insulation covered by a black surface that absorbs radiation.

In this module, sufficient seawater is pumped in to achieve a pool depth of 5 to 30 cm. A small portion of the solar radiation is reflected off the roof, the pooled seawater absorbs another portion, and the remainder is captured by the black surface, which heats up the seawater to produce steam. The lower-density steam and hot air mixture rises, condenses on the cooler glass roof, and slides down the inside of the roof to collectors installed along module walls. After the vapor condenses on the glass, the air cools,

gains density, and descends. Upon reaching the water, it becomes moisture saturated, and the entire cycle is repeated.

Periodical purges are done to prevent salt sedimentation that lowers system productivity.

The entire process is based on an energy balance, whereby all losses not used to heat the seawater are subtracted from the energy received through solar radiation.

The passage of solar radiation through glass is verified as depicted in *Figure 5*. The losses indicated in the figure reflect only part of the picture. Other losses occur due to reflection on the (less than ideal) black surface, thermal radiation of the water, and heat loss through the flooring. These losses can be reduced through the proper selection of materials and layout.

The main problem with this type of plant is the large surface area required to obtain significant amounts of water. This is because solar radiation reaching the earth´s surface is low density, which makes for low energy capture per square meter.

Figure 6 depicts the curve for liters of potable water obtained per square meter per day, adjusted for pool seawater levels and time of day needed to achieve ground measured solar radiation of $4,090$ Kcal/m^2/day, the average radiation value for the province of Almeria, Spain. As seen in Figure 6, a pool with 15 cm. of seawater would produce 6.5 l/m^2 per day. In other words, a dedicated surface area of 153 m^2 is required to obtain 1 m^3/day of desalinated water.

Production is highly dependent on climate and seasonal changes, which precludes use of this process for large-scale needs. However, it can prove a viable potable water solution for areas lacking other energy sources and/or the skilled personnel needed to manage a more complex desalination plant.

Experimental plants of this kind exist in Australia, Chile, Aldraba Island in the Indian Ocean, Patmos Island (Greece), and the Pacific Isles.

DESCRIPTION OF PRINCIPAL MEMBRANE BASED DESALINATION PROCESSES

Reverse Osmosis

Figure 7 shows two connected recipients separated by a semi-permeable membrane, penetrable only by water. If we fill the left side with purified water, and the right with water containing dissolved salts, osmosis occurs as the purified water exerts pressure on the membrane, and its molecules pass through the membrane to reach the saline solution to lower the concentration. No molecules of the saline solution move to the purified water, rather, the number of water molecules permeating the membrane move to the saline solution. This is osmosis, a process by which fresh water is lost and the quantity of salt water increases until the differential water column between both receptacles achieves equal osmotic-hydrostatic pressure, which apparently ends the process, as shown in *Figure 8*. What really happens is that once the osmotic-hydrostatic pressure is equal on both sides, equal numbers of water molecules of both types move freely back and forth, in a state of equilibrium.

If, using the same process depicted in *Figure 8*, we insert a plunger to exert mechanical pressure on the saline solution surface, the balance is reversed, and more water molecules migrate from the saline solution (right recipient) to the purified water (left recipient). Figure 9. In other words, we obtain purified water from the saline solution. This is reverse osmosis, the process used to desalinate brine and seawater.

Simplified diagram of a reverse osmosis plant

Figure 10 is an overview of an RO plant depicting the most practical way to use this process in industrial settings.

Intake pumps send seawater and brine to sand filters that eliminate suspended matter of up to 50 micras, from where it then goes through microfilter cartridges for refiltering down to less than 10 micras. From here a high pressure pump provides the pressure needed for reverse osmosis to take place. To give an idea of the amount of pressure required, note that seawater has an osmotic pressure of between 25 - 30 bars, and the working pressure of the membranes is between 65 - 70 bars, i.e., 2.5 times the osmotic pressure. This is because during reverse osmosis, seawater concentrates inside the membranes and raises their osmotic pressure, due to which the salt concentration of the rejected salty water is nearly double that of the seawater, making for an osmotic pressure of 55 - 60 bars. For briny waters, the working pressure depends on the type of dissolved salts and their concentration levels, and calls for a case by case determination of the optimum working pressure for the membranes, which in practice, varies between 8 - 30 bars. One important design parameter for this type of installation is the 'conversion factor', which is obtained by dividing the flow of product water by that of the feedwater entering the membranes. The final conversion factor will depend on the types of dissolved salts, the pretreatment used, and the maximum admissible concentration before salt precipitation occurs. The conversion factor for seawater is between 45 - 55%, which means that between 45 - 55 m^3 of product water is obtained from each 100 m^3 of seawater passing through the membranes. Conversely, for briny waters the conversion factor can be up to 85%.

The salty water issued from the membranes after reverse osmosis retains considerable pressure, having released only 2 - 3 bars during the R.O. process. The brine is then circulated into an energy recovery system involving either back-pumps, Pelton or Francis turbines, or a pressure exchange system (P.E.S.) that take advantage of the pressure surge occurring as the pressurized brine leaves the membranes and hits lower air pressure in its gravity propelled journey down to the sea. Recovery makes for a considerable reduction in process energy requirements.

Because the membranes used in reverse osmosis cannot achieve 100% salt rejection, the product always retains a certain amount of salt. Concentrations vary, depending on those

of feedwater, brine conversion factor, water temperature, membrane type and design. For seawater it is usually 200 - 300 mg/l. to lower product water salt content further, a two step plant is needed.

Figure 11 is a simplified diagram of a two step reverse osmosis (RO) plant. Here, a pump raises the pressure of the product water from first stage osmosis to 6 - 8 bars, and sends it to the type of RO membranes used for brackish water. This second stage lowers product water salt content to 10 mg/l. Second stage conversion factors tend to be very high, around 90%. Second step reject water is recombined with first step raw feedwater.

Electrodialysis

Salts dissolved in water split into ions, which are negative or positive atomic or molecular particles. For example, common table salt - sodium chloride- ionizes to form both positive (cation) and negative (anion) charges, (Na+) and (Cl-), respectively.

The difference between electrodialysis and reverse osmosis is that, while in R.O., what moves is the water, as it permeates the membranes and leaves behind concentrated salt water, in an electrodialysis plant, what moves are the ions of dissolved salts that leave no salt solute behind.

In a field of continuous current, the positive ions, known as cations (Na$^+$, Ca^{2+}, Mg^{2+} etc.), are attracted to the negative pole or cathode, and the negative ions, which are called anions (Cl$^-$, SO$_4^{2-}$, CO$_3$H$^-$, etc.) to the positive pole.

Electrodialysis units monitor ionic transfer via cation/anion resin membranes.

Cation membranes are negative and repel anions (like sulphonates). Thus, cationic membranes (highlighted in yellow, *Figure 12*), transfer cations like Na$^+$, Ca^{2+}, Mg^{2+} but not anions. Conversely, anionic membranes (highlighted in pink, *Figure 12*) contain positive charges (similar to those of quaternary ammonia) that repel cations while allowing the transfer of anions like Cl$^-$, SO$_4^{2-}$ and HCO$_3^-$.

Figure 12 is an illustration of a traditional electrodialysis or "stack" plant using a combination of all the elements

described above (ions, selective anionic and cationic membranes and continuous field) to achieve demineralization and flush ionic concentrations out in reject waters.

Successive membranes are installed interspersed with 1 mm spacers, to form what is called a paired-cell array, comprised of:

- A cationic membrane
- A cationic membrane spacer
- An anionic membrane
- An anionic membrane spacer

The feedwater with dissolved ions is pumped to the membrane stack, where it is circulated through the cationic and anionic membranes.

When continuous current is applied, the cations move toward the negative pole. If the first membrane encountered is cationic, it passes to the next compartment, partially demineralizing the previous one. However, if the first membrane encountered is anionic, the ion does not pass through it, and it will be a concentrate compartment.

As seen in *Figure 12*, the anions are attracted to the positive pole, and undergo the same movements and subject to the same restrictions as the cations, but in the opposite direction.

So, in an electrodialysis layout of alternating cationic and anionic membranes, each ion can permeate a maximum of one compartment before being blocked by the corresponding membrane.

The net result of the ion movement through the membranes is that one of the groups of water compartments will be demineralized and the other will become concentrated. At the end of the "stack" the water from the demineralized cells is pumped out as product water. The water from the cells where the salts have concentrated is also extracted. Part of it is mixed with the intake water and the mixture is reintroduced in the concentrate cells. The other part of the concentrate is sent to reject as brine purge to maintain the salt balance inside the "stack" and keep more water from gradually concentrating inside. The raw water feed pumps pump

water into the cells where most of it will become demineralized, and the other part will be mixed with a portion of the concentrate, as explained above.

The system described is a classic example of unidirectional electrodialysis. It is called unidirectional because polarity does not change, so the ions always move in the same direction, and the basic characteristics of the individual water cells remain unaltered: they will always be either dilute or concentrate cells.

The classic unidirectional system was the first electrodialysis process developed. However, the unidirectional ED process had some limitations that were partially overcome through the change to Reversible Electrodialysis, because during RE polarity reverses at given intervals, during which the product cells become concentrate cells, and vice versa.

Nanofiltration

Nanofiltration, a process mid-way between ultra filtration and reverse osmosis, uses semi permeable membranes with pores of 0.0001 - 0.001 micras, i.e. smaller than a nanometer, which reject molecules with an organic weight exceeding 200 Daltons. One distinguishing characteristic from reverse osmosis is that it rejects 30 - 60% of monovalent ions, and 90 - 98% of divalent ions, which enables very low pressure operation (4 - 12 bars, depending on water type). It generally uses spiral membranes with an active layer of polyamide, and polysulphone and polyester support layers. Other nanofiltration membranes available on the market include active layers of poly vinyl alcohol and sulfonated polysulfate, in spun spiral or hollow fiber configurations.

While most frequently employed in surface water treatment to eliminate manmade organic materials (plaguicides), naturally occurring organic materials (humic acids), overall hardness and calcium sulfate, it is also used for pretreatment in evaporation desalination systems, to reduce calcium sulfate content, raise maximum operating temperatures, and avoid salt precipitation.

Nanofiltration systems have much in common with reverse osmosis membrane systems, but for nanofiltration, good

feedwater pretreatment technology is essential to keep colloidal particles from clogging membranes and avoid chemical precipitation, and so eliminate frequent downtime for cleaning. The operating scheme is identical to that of a reverse osmosis plant, except that while reverse osmosis rejects almost equal percentages of all salts, nanofiltration rejects more divalent than monovalent ions. Nanofiltration uses less energy than reverse osmosis per cubic meter of production water, but is only applicable for waters having a high divalent salt content.