

Trabajo Fin de Máster

Máster universitario en Sistemas de Producción de
Potencia

Concentrate treatments in reverse osmosis
desalination plants: Status and innovative proposals

Autor: Eva Sánchez Carceller

Tutor: Lourdes García Rodríguez

Dpto. Máquinas Térmicas
Escuela Técnica Superior de Ingeniería
Universidad de Sevilla

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Autor:

Eva Sánchez Carceller

Tutor:

Lourdes García Rodríguez

Profesor titular

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El tribunal nombrado para juzgar el Proyecto arriba indicado, compuesto por los siguientes miembros:

Presidente:

Vocales:

Secretario:

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A ellos,

Abstract

The rise of the population growth with the pass of the years cause the rise of raw materials such as water. Because of supply this huge demand for fresh water, the desalination plants increase the brine flows discharged, which causes a greater environmental impact. This project aims to carry out a study of the management of brines from the rejection of desalination processes by reverse osmosis. A collection of different bibliographic sources and an investigation of the state of art in this field is carried out, delving into the most common aspects, such as the direct elimination of reject brines, the minimization of them and, finally, their reuse.

The range of the project encompasses the bibliographic search, the drafting of the most interesting and important points in it and, finally, a simulation in MATLAB of a system that reuse the exhaust gases of a microturbine to increase the salinity of a brine.

Índice

Abstract	xiii
Índice	xv
Índice de Figuras	xviii
1. Introduction	1
1.1. <i>Background of desalination water</i>	1
1.2. <i>Current trends in brine disposal</i>	2
1.3. <i>Objectives and range</i>	4
2 Brine management methods	5
2.1 <i>Brine minimization</i>	5
2.1.1 Chemical pretreatment	5
2.1.2 Electro kinetic treatment and ionic exchange	6
2.1.3 Biological techniques	7
2.1.4 Vibratory Shear Enhanced Processing (VSEP)	7
2.1.5 ED, EDR and EDM (Electrodialysis Metathesis)	8
2.1.6 Forward Osmosis (FO)	10
2.1.7 Wind-aided intensified evaporation (WAIV)	11
2.1.8 Brine Concentrators (BC)	12
2.1.9 Ohmic evaporator	13
2.1.10 Brine crystallizer	13
2.1.11 Multi-effect Distillation (MED) and Mechanical Vapor Compression (MVC)	14
2.1.12 Membrane Distillation (MD)	14
2.2 <i>Direct removal of brines</i>	16
2.3 <i>Reuse application of reject brine</i>	17
2.3.1. Chemical precipitation	18
2.3.2. Adsorption	18
2.3.3. Membrane and electrokinetic processes	19
2.3.4. Crystallization and evaporation	20
2.3.5. Regeneration of wetlands and agriculture applications	21
3. Brine concentration	23
3.1. <i>Matter balance</i>	24
3.2. <i>Energy balance</i>	24
3.3. <i>Each current data</i>	26
4. Conclusions	28
4.1. <i>Effect of T_1 y T_2 in the mass flow m_3</i>	28
4.2. <i>Effect of T_1 y T_2 in the salinity S_3</i>	29
4.3. <i>Effect of m_2/m_1 ratio in the mass flow m_3</i>	30
4.4. <i>Effect of m_2/m_1 ratio in the salinity S_3</i>	31
4.5. <i>Effect of S_1 in the salinity S_3</i>	32
Bibliografía	33

Índice de Figuras

Fig. 1. Changes of bottled water consumption in Spain (thousands of m ³) [1]	1
Fig. 2. Simple Seawater desalination process by Reverse Osmosis (SWRO) [108]	3
Fig. 3. Mass flow in a common desalination plant [3]	3
Fig. 4. General Electric's Aquasel NTBC	9
Fig. 5. Brine concentrator functional layout	12
Fig. 6. System diagram	23
Fig. 7. m_3/m_1 tendency with T_1, T_2 variations	28
Fig. 8. S_3/S_1 tendency with T_1, T_2 variations	29
Fig. 9 m_3/m_1 evolution with T_1, T_2 and $m_2/m_1=0.1$	30
Fig. 10 m_3/m_1 evolution with T_1, T_2 and $m_2/m_1=0.2$	30
Figura 11 S_3/S_1 evolution with T_1, T_2 and $m_2/m_1=0.1$	31
Figura 12 S_3/S_1 evolution with T_1, T_2 and $m_2/m_1=0.2$	31
Figura 13 S_3/S_1 evolution with T_1, T_2 and $S_1=0.07$	32
Figura 14 S_3/S_1 evolution with T_1, T_2 and $S_1=0.085$	32

1. INTRODUCTION

The water demand on all civilized countries has risen due to the population growth with the pass of the years (Fig. 1). This fact is undoubtedly related with the increase in brine flows discharged by the desalination plants, which causes a greater environmental impact.

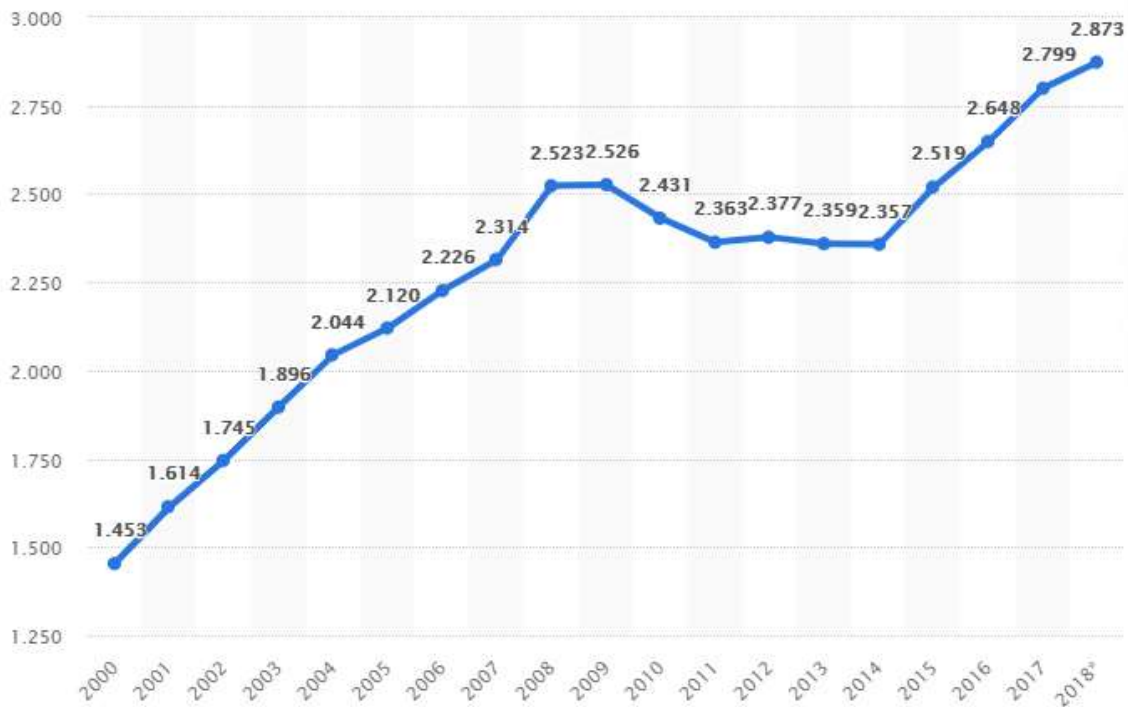


Fig. 1. Changes of bottled water consumption in Spain (thousands of m³) [1]

Therefore, and more than ever, is necessary to correctly manage the brine discharge of the desalination processes, in order to achieve a correct disposal of the output, brine minimization or an efficient reutilization of this.

Many investigations came out because of this, with the objective of reducing the brine disposal of the desalination plants. The management processes consist, commonly, in minimization techniques that use various technologies, such as membranes to do physical-chemical separations, heat treatment methods (distillation, vaporization, etc.) and some innovative technologies that are appearing nowadays.

This project also makes a point about the process sustainability showing up different ways of brines disposal and even other applications that the output may have, promoting its reuse.

1.1. Background of desalination water

Reverse osmosis on desalination process of seawater is one of the biggest sources of drinking water of the world. Sea Water Reverse Osmosis (SWRO) or Brackish Water Reverse Osmosis (BWRO), the reverse osmosis is a fairly normalized process at the current industry, and it is present in most of countries without natural sources of fresh water.

The ancient background of the process makes that the optimization no longer focus on the process

itself, instead of that, it is searching for a better energy efficiency, a better separation processes or low fouling and scaling.

The continuous upgrades and optimizations of this method have made of this technology something solid and economical, largely replacing other processes for obtaining drinking water like industrial distillation, which needs more expensive equipment, bigger and with low operating flexibility.

During the past decades, the SWRO technology has greatly risen its production capacity, in 2011 the global processing capacity up to $3.5e^7$ of water each day. In addition to optimizing energy consumption, reducing it by a large percentage, from 20 to 2.5 kWh (approximately) per m^3 of treated water [2].

The RO is so extended due to its capacity to be useful in a lot of different situations, this technology is not only used for desalination processes. The wide use and versatility of the RO has made this process studied for use in very promising fields for the industry. The membrane technology can be used, for example, to obtain molecular hydrogen, separating it from the other components of the flow [3]. Another possibility is the use of palladium based or ceramic membranes, useful for ionic transport or CO_2 catching on natural gas treatment. There are, also, more applications of this technology at the pharmaceutical or biotechnological fields isolating amino acids, proteins, or enzymatic substances.

All this history and the actual possibilities in this technology makes it remain on the spotlight of current industry, being a constantly improving and optimizing process.

1.2. Current trends in brine disposal

In nature, water is found in three different states: solid, in the form of ice; gaseous, like steam in the atmosphere; and liquid, as the water of rivers, lakes and seas. However, of these three states, only the ice can be considered like pure water. The liquid state of water is impossible to find in the nature, and the drinking water is, in fact, a solution of salts using water as solvent element. The taste of drinking water depends on the composition of salts that it has diluted. In this way, the water prevenient from coastal zones will had a different, and generally worst, flavor than the water at the mountains, with less concentration of salts.

Therefore, water solutions found in nature can range from 0.2 grams per liter of salts in mountain water, to about 35 grams per liter on average in seawater. In other way, the salts concentration in output brines can achieve the 45 grams per liter, which are dumped directly to the ocean.

In order to obtaining drinking water from seawater it is necessary to reduce the salts concentration in seawater under 0.5 grams per liter. This objective is pursued by the desalination plants of reverse osmosis (RO), getting a waste current from the membranes reject flow. This reject flow is a dissolution of seawater highly concentrate in salts (Fig. 2).

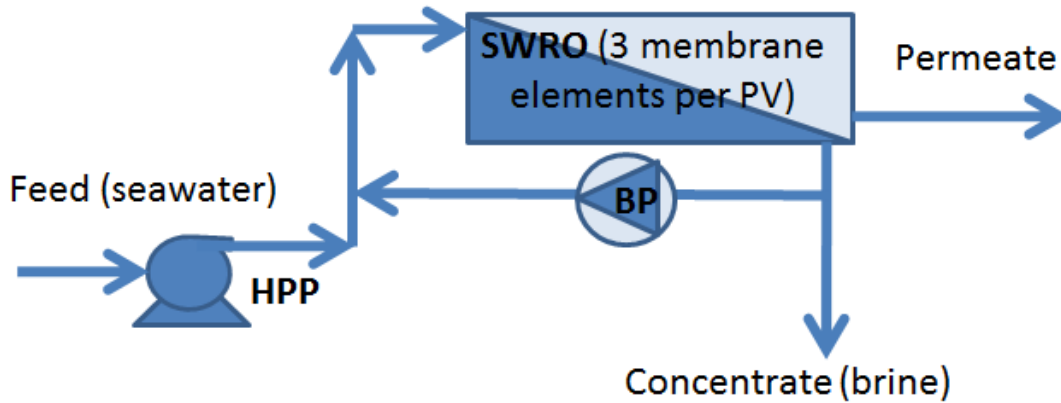


Fig. 2. Simple Seawater desalination process by Reverse Osmosis (SWRO) [108]

In the previous image can be seen the feed flow (the seawater), the permeate flow (the product of the process) and the concentrate flow (the brine).

As usual, it is obtained a 50 % of drinking water of all the seawater fed to the plant. Because of that, something more than a half is treated as waste, and is bumped to the sea as brine flow. For example, if some plant were fed with 1 L of seawater, it would produce 0.45 L of drinking water, approximately, and 0.55 L of brine. Focusing in a desalination plant placed at Alicante, Spain, it is obtained the next flow scheme (Fig. 3):

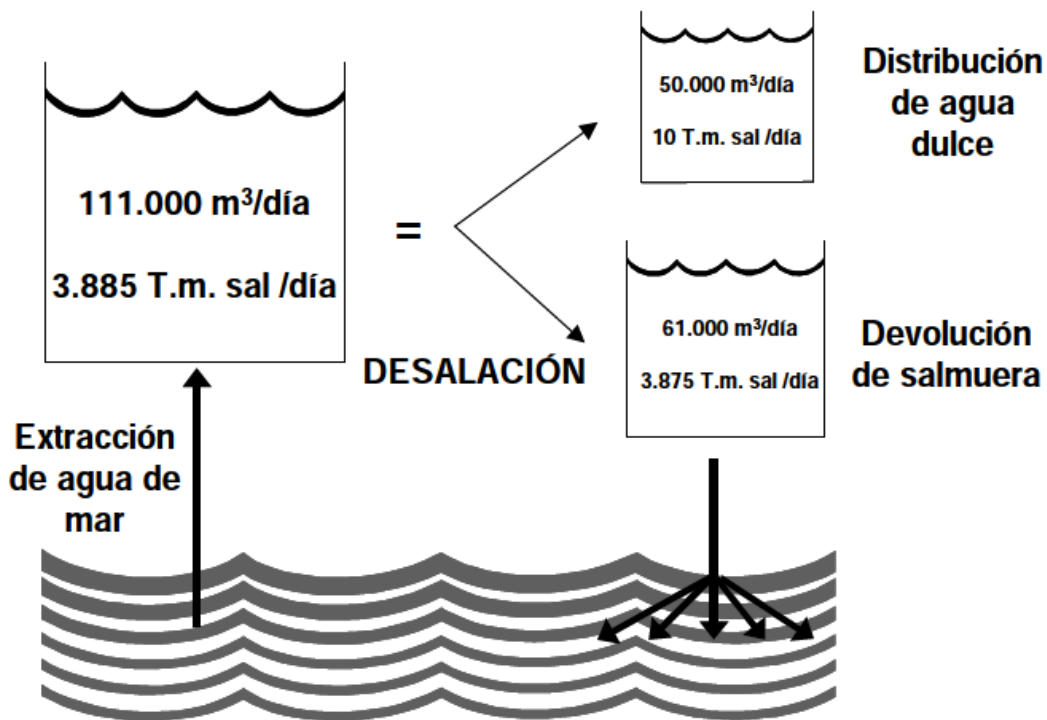


Fig. 3. Mass flow in a common desalination plant [3]

Some studies from 2017 [4] confirm that almost 76 million m³ of brine water per day are produced by desalination plants, although nowadays this figure can be larger.

It is obvious to come to the conclusion that it is necessary to study a method that considerably reduces the brine flows thrown into the sea by desalination plants. A reducing method based on the elimination or, better still, the reuse of the waste stream.

1.3. Objectives and range

This project aims to carry out a study of the management of brines from the rejection of desalination processes by reverse osmosis. A collection of different bibliographic sources and an investigation of the state of art in this field is carried out, delving into the most common aspects, such as the direct elimination of reject brines, the minimization of them and, finally, their reuse. The latter alternative is the most interesting and the one with the most prominence in this work.

The range of the project encompasses the bibliographic search, the drafting of the most interesting and important points in it and, finally, a simulation in MATLAB of a system that reuse the exhaust gases of a microturbine to increase the salinity of a brine.

2 BRINE MANAGEMENT METHODS

Desalination technology is widely used in places where drinking water resources are limited, an example of this is Middle East and, specially, the United Arab Emirates (UAE). The environmental issue generated by the desalination processes around the world is one of the biggest cons in the production of fresh water from desalination plants based on either, distillation and SWRO processes [5]. This is mainly due to three causes: chemical products added to the mainstream of the process that keep existing in the waste flow; high temperature (only in distillation plants) and salinity in the blowdown (brine), much higher than the environmental ones.

On the other hand, the outlet properties can be highly modified by the quality of the water fed to the plant. Depending on the quality of the water resources different previous treatments or other steps in the process would be necessary to achieve the adequate product properties.

The main damages of reject brine to the environment include eutrophication, pH fluctuations, incrementing concentration of heavy metals and sterilizing characteristics due to the disinfectants which can cause a series of problems to marine and underground habitat [6].

In order to achieve the best way to manage reject brine, it has been considered different factors like total reject flow, the composition of the reject flow, the ubication of the desalination plant, etc. [5]. All of this makes the management of the project very difficult and expensive.

There are different reject brine management strategies: brine minimization, direct disposal, or direct reuse. This project aims to investigate these three strategies.

2.1 Brine minimization

The desalination plant rejects large volumes of brine because the present technology can't achieve the complete recuperation of the permeate [6]. It is a priority to focus on this field through the treatment of the brine itself, attempting to reduce its volume.

2.1.1 Chemical pretreatment

Chemical pretreatment is commonly used for the removal of scaling or inorganic components such as Ca^{2+} , Mg^{2+} , Ba^{2+} and Sr^{2+} , before the secondary treatment of the flow. The advantage of this method is found in the high recovery of the permeate (> 95%). Some studies [8] have achieved a very high recovery of the permeate with this method, obtaining up to 83% recovery in the first step and more than 95% in the second.

In other way, it is necessary a chemical pretreatment to the brine after the first step of the process, to obtain a better recovery and a bigger reduction of the volume in the end of the process. This second treatment is also due to the high concentration of chemical compounds that the flow is bringing with itself from the first step, these chemicals can damage the membrane of the second step or reduce the efficiency of the process. This "post-treatment" can enhance the recovery from an initial 85 % up to a 95 % with a second step. Moreover, with this method the scaling precursors such as Ba^{2+} , Ca^{2+} and Sr^{2+} were eliminated in a solid contact pilot-scale reactor in a 67, 97, 94 and 88 % respectively.

This RO two-step process with an Intermediate Chemical Demineralization (ICD) was used to minimize the reject and enhance the permeate recovery of the brackish water in Colorado River, in the Unites States [8].

During the ICD step, the scaling precursors can reach a high concentration, seriously exceeding their solubility and making very difficult the pH control. Rahardianto et al. [7] offers a solution to this problem through the incorporation of a Accelerated Precipitation Softening (APS) system between the first and the second step. The “APS” system involves a pH adjustment to the alkaline range (10.5) through the addition of Sodium Hydroxide (NaOH) followed by the seeding of calcite crystals. This process ensures the solution desaturation of the scaling precursors. The seeding of the crystals is also followed by microfiltration and normalization of the pH by HCl addition before the secondary step to prevent calcite scales formation. The demineralization of the solution enhances the efficiency of the process from a 90 % up to a 98 % of global recuperation. The “APS” also reaches the reduction of compounds like Ba, Ca, Sr, Mg/Si in a >95, >90, 78 and 10-20 % respectively [9].

2.1.2 Electro kinetic treatment and ionic exchange

Electro kinetic separation is a new method used to achieve softening (mineral concentration reduction) of primary brines before the secondary step of the RO [10, 11]. Electrocoagulation is one of the purification methods in electro kinetic applications [12, 13].

Electrocoagulation is a process that changes surface charge of particles by continuously providing metallic ions as coagulant sources with the aid of a sacrificial anodic electrode [14-16]. Such anodic electrode expels a continuous source of metallic ions, forming metal hydroxides that destabilizes the floating particles. At the same time, an electrophoretic process leads a negatively charged particles current to the anodic electrode surface. By this way, attraction forces were created between the anode and the charged flocs in the diffuse layer, and, subsequently, charged particles become deposited on the electrode. During this process, some flocs reach the necessary weight to gravitational precipitation.

This system has generated great advances in RO processes, going to be called "high efficiency RO systems", for example, by electro kinetic pretreatment 80% of silica of brackish water has been eliminated using a current of 0.5A and an hydraulic retention time of 30 minutes [17]. Another example is in the water treatment of Big Bear Valle, California, where permeate recovery has been significantly improved thanks to a high-efficiency RO system [18].

A proposed improvement to join electro kinetic systems consists of the filtration and recycling of concentrate. Sometimes the concentrate treated after the last step is filtered and recirculated to the intermediate step between the stages of the process, where it can be reused as second-step feed water (brackish water). Various simulations have shown that with this system a very high recovery can be achieved (from 99.5 to 99.9%). However, this method does not eliminate the hardness of the current, since the recirculated current implies a high salinity, which makes the process possibly unprofitable [19].

On the other hand, ion exchange has also been used to remove silica and silicate from nanofiltration concentrate (NF) [20, 21]. Bivalent ions, such as calcium, barium or magnesium are removed with this method to prevent the formation of scales during filtration process. With this system, a 98% permeate recovery is achieved. However, by using this methodology forms a layer of fouling composed, among other compounds, by silica, aluminum and iron, which reduces the percentage of effective recovery of the membranes after washing and makes it necessary to carry out more studies and tests to verify their long-term economic validity.

Finally, it is worth mentioning that the Electrodialysis Reversal system (EDR) is suitable for high efficiency when is applied as pretreating [22]. EDR can achieve maximum recoveries of up to 92-94% for one-step systems and up to 97% in two-step systems [22], resulting in a huge decrease in concentrate flow, which can be poured, treated, or reused.

2.1.3 Biological techniques

Biological pretreatment techniques have proven to be viable ways of removing some foulants or scalants from low-salinity brine.

A biological process using sulfate reducing bacteria has been tested to reduce the sulfate content in the RO concentrate [23]. To effectively remove sulfates through these bacteria, it is necessary both an electron donor and a carbon source, in a study taken as an example [24], acetate is used as an electron donor. One option for the reduction of sulfates by biological means is the use of a Fluidized Bed Bioadsorber Reactor system (FBBR) [25].

The source of feed water is water from the Colorado River in Southern California, with a TDS over 700 mg/L. With this kind of water the reduction of sulfate is a priority to improve the overall recovery of permeate, as well as for the reduction of the precipitation potential of barium sulfate, calcium sulfate and/or strontium sulfate in the membrane, during the second step of the process [25]. It is demonstrated that FBBR is an effective and cost-effective technology that can be used to remove sulfate from the concentrated stream of an RO, with a recovery greater than 95% [25].

However, if heavy metals (which inhibit microbial activity by poisoning them) are majority components in the composition of brine concentrate, it would be convenient to look for an alternative to the use of FBBR. A resolution to this problem could be, for example, granulated active carbon that can adsorb such heavy metals, resolving the problem [25]. The FBBR has also been used to remove ammonia content from the concentrate of a RO process with the aim of reducing the components dissolved in it by denitrification [26].

As an experimental method, brackish water product from a RO process was treated with a biological method. Using a biological willow bed and, as a feeding stream to the system, a previously treated effluent of wastewater [27]. In this experiment, total COD, nitrogen, and phosphorus were eliminated by 20, 32 and 32%, respectively. After this biological treatment, an electro dialysis system is added, with the aim of treating the rejection concentrate, which is redirected back to the wastewater treatment plant. This technique ensured a high total recovery of permeate water, a minimization of waste brine and the transfer of xenobiotics in the final concentrate discharged to the wastewater treatment plant, rather than sending all of that, directly, to the environment.

2.1.4 Vibratory Shear Enhanced Processing (VSEP)

Vibration Shear Enhanced Processing (VSEP) is a technology consisting of surface oscillation of the membrane and is used to improve membrane-based minimization strategies [28, 29].

A system to treat the concentrated flow from a RO process in a VSEP unit is designed, using the classic plate and frame configuration [28, 29]. The mechanism by which the system operates consist in the application of a vibrating shear performed by torsional oscillation at 50 Hz frequency in the membrane surface, so that the shear size is ten times larger compared to the typical cross-flow membrane systems [29].

Through this method a significant reduction of brine final volume is achieved and prevents polarization and colloidal fouling by creating a considerably shorter route for feed water across the membrane surface thanks to the vibration produced.

Unlike conventional RO processes, VSEP is not limited by salts composition and concentration in the treated flow, the presence of suspended solids or colloids in the brine. Therefore, the great advantages of this method are the high resistance to membrane flake, the high filtration rates, and the low decrease of effective area in the membrane [30]. On the other hand, the energy to maintain active vibration is

something to consider.

As an experimental study, an example is given with high flows (50-100 L/m²-h) treated by VSEP for the concentrate of the first step [29]. In this case, colloidal silica deposition in the membrane decreases as a result of the vibrating shear [30]. However, precipitation with barium sulfate is not controllable and a frequent chemical cleaning is necessary. Implementing continuous cross-flow operation reduces "scaling" and improves total permeate recovery (from 75% to 93%).

Another case studied is obtained from the Kay Bailey Hutchison brackish water desalination plant (KBH) in the United States. By using VSEP, up to 80% of the concentrate can be recovered. The disk tube (DT) configuration of the NF membrane, which is similar to VSEP (except for the torsional oscillation on the membrane surface), has also been used to achieve different recoveries ranging from 50 to 80%, for a flow of 30-34 L/m²-h [31]. In this case, high recoveries are achieved because the application of chemical cleanings and periodic washing with RO permeation is eliminated.

2.1.5 ED, EDR and EDM (Electrodialysis Metathesis)

Treatment processes induced by electrical potential have been combined with membrane-based systems to minimize brine volume and remove embedding ions from it. Thanks to this, interesting results have been obtained in the treatment of brine rejection by membranes. Of all the treatments with electrical potential for rejection reduction, three stand out as main: ED, EDR and EDM [32-37].

These processes use the electrical potential to allow the movement of dissolved ions through waterproof ion exchange membranes. Cations and anions can move through the membrane, leaving the water on the opposite side of it.

Electrodialysis (ED) consists of positioning batteries of selective ion membranes between electrodes. The cations move towards the negatively charged cathode, while the anions move towards the positively charged anode. This system is feasible to treat low to moderate salinity osmosis concentrates at a relatively low cost. However, one of the main problems in this system is the scaling, which can occur within 80 minutes of operation needed to reach the maximum voltage if calcium is present. On the other hand, a pellet reactor included as a pretreating stage can solve this problem [33], reaching a calcium removal of 70-80 % (under pH=11 conditions [33]), although if the pH is still increased to 11.5, the elimination efficiency reaches 95%. Magnesium removal efficiency under these same conditions is between 5 and 25%, not a very high value.

EDR is similar to the ED, with the difference that the direct current voltage is reversed 3 to 4 times per hour and allows to achieve a total recovery of the permeate of up to 97% [38]. This system is often combined with other brine treatment technologies, such as the combination of ion exchange with EDR for the removal of flake-forming ions, coupled with the treatment of RO concentrate has resulted in a full recovery of approximately 98.9% of the permeate [37]. General Electric has also achieved 99% water recovery through Aquasel's Cold Brine Concentrator (Aquasel's Non-Thermal Brine Concentrator, NTBC) for the treatment of RO concentrate, using a two-stage process of EDR and precipitation [39]. The feed water in this study is the process waste effluent of a bottling plant. The water produced in the first stage, EDR, can be recirculated to the first step feed with the aim of reducing the general water consumption (Fig. 4). Brackish water is further concentrated in the second stage, thanks to a precipitation unit, where solid salts are obtained in the form of a precipitate and permeate is recirculated at the entrance of the EDR to reduce the salinity of the EDR.

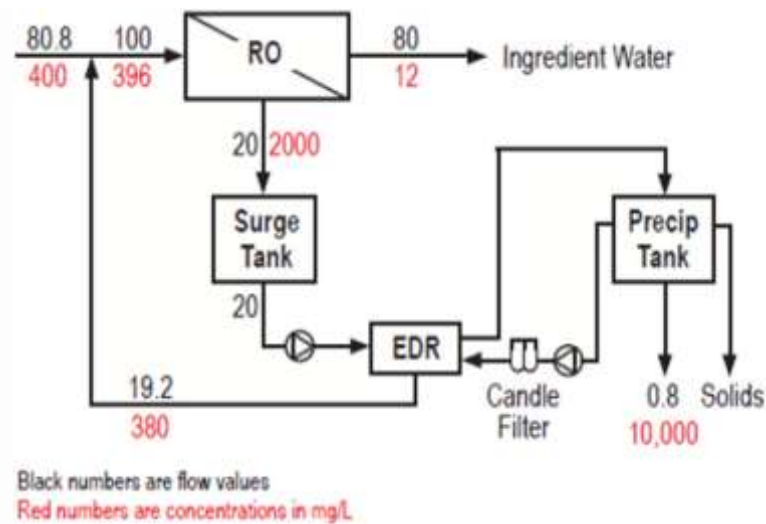


Fig. 4. General Electric's Aquasel NTBC

EDR system has also demonstrated to be effective for precipitation of gypsum, calcium sulfate and barium sulfate from brackish water, as well as to prevent the formation of inlays when integrated with a crystallizing precipitator [35].

Mathematical modeling of these processes yields results that the ED-RO configuration delivers better permeate recovery and lower specific power consumption compared to the traditional RO process.

EDM system has been tested to maximize water recovery and produce concentrated salts from rejected brine, with EDM being a conventional ED modification. An EDM stack containing ion exchange membranes and solution thin layer compartments has been used to treat concentrated brine produced by a conventional RO/NF [40] system. EDM process consists of four ion exchange membranes used in a repeated unitary cell, the metathesis processes in EDM are used to remove salts in a similar way of a human kidney. Using EDM to desalinate brine from RO, the process generates one permeate current and two EDM concentrate currents. Thus, the main difference between EDM and ED is that the ion exchange membranes are arranged in such a way that the brine is separated into two concentration currents.

Bond et al. [41] demonstrates that the EDM process can also be used to achieve ZLD desalination using brackish concentrate [41]. This study is conducted to treat concentrated NF, RO and EDR samples from four desalination plants. The most relevant operational variants in this experiment are flows, pressures, voltage, and current in power and concentrate tanks, and electrolytes. Total Dissolved Solids (TDS) reach concentration ranges ranging from 3000 to 16000 mg/L in concentrate samples. From the separation produced by the EDM are two currents with highly soluble salts, which have a different composition each. The first contains high concentrations of sodium, chloride, and sulfate with low concentrations of calcium and magnesium, while the second, on the other hand, has high concentrations of chloride, calcium, magnesium and sodium. Pilot tests achieve between 99.8% and 99.9% recovery, while EDM power consumption ranges from 1.1W to 1.8 W per cell.

Considering the obtained energy consumption and the recovery of the process, the specific cost for this system is lower than that of the ZLD thermal process. The cost of implementing ZLD treatment through EDM, followed by a crystallizer for optimal water recovery and solid salt collection can range from USD 0.64 to USD 11.21 per cubic meter of recovered water [41]. However, this cost is shown to depend on power TDS. In addition, the EDM process is not affected by any membrane fouling.

2.1.6 Forward Osmosis (FO)

FO is a very useful water treatment technique for both water desalination and brine rejection management [42, 43]. In this process, the water molecules in the feed solution are less concentrated, and therefore go towards a more concentrated solution, which is called an extraction solution, reaching it through a semipermeable membrane. This membrane allows the concentrate to pass through but retains the ions and most solute molecules. Due to the osmotic difference between the two solutions, the feed solution has a reduced osmotic pressure, while that of the extraction solution is superior. The water is transferred to the extraction solution, diluting it and, in turn, concentrating the feed current.

To maintain this driving force, the solvent flow must be reconcentrated, the FO process depends largely on the choice of extraction solution, because it affects the osmotic driving force that will generate the osmosis process [44, 45]. The extraction solution must have considerably high osmotic pressure compared to the feed solution in order to maintain the driving force of the mass transfer. In addition, it is a convenient requirement that water be separated from the extraction solution for easy recirculation before the FO process can be finished.

The main advantage of FO is that it requires less energy for the extraction dilution step than its opposite, RO, as it is based on a natural osmosis phenomenon, which occurs spontaneously. In addition, the fouling of the FO membrane is not considered a major problem because no hydraulic pressure is required to carry out the process. In most cases, FO membrane fouling can be reversed by washing with water, indicating that chemical cleaning may not be necessary in some cases.

The main drawbacks of this technique lie in the lack of improved and durable membranes with specific designs for the diversity of cases existing in the industry, the energy requirement for the regeneration stage of the extraction current and the lack of availability of effective extraction solutions that limit the use of FO for brine rejection treatment [45].

In addition, in this kind of process it is necessary to consider a factor that can be harmful to the process. This factor is the polarization of concentrate (PC), this phenomenon can occur internally, forming on the porous support side, as externally, occurring in the active layer of the membrane. The PC may be responsible for decreasing the total performance of the process [45].

Although fouling may be lower in FO processes due to the absence of applied pressure, inlays of poorly soluble salts may occur [46].

In order to correctly determine the properties of this system, the performance of three FO pilot plants has been compared with the Mechanical Vapor Compression (MVC), Membrane Distillation (MD), and Multi-Stage Flash (MSF) processes to demonstrate the overall efficiency of an FO brine concentration system [47]. With this experiment, IT is shown that FO pilot plants are energy inefficient, however, by optimizing the mass flow ratio, FO energy consumption can be reduced by 3% in Nicoll's FO-RO model and by 21% in the thermal model.

FO has been used to treat different reject brines resulting from RO desalination of brackish water from a plant in the United States [44]. The first brine (brine A) was generated from the RO plant with a concentration of TDS of almost 7500 mg/L, while the second brine (brine B) was generated from the treatment of brine A by softening and Electrodialysis Reversal (EDR), and with approximately 17500 mg/L of TDS. As a result of the treatment, B brine had more TDS, more sodium ions and more chloride ions, but fewer concentrations of silica, sulfate and calcium due to softening pretreatment. The FO method was tested on both brines using a test unit connected to a pilot-scale RO unit. The extraction solution is produced with a stable concentration of NaCl

(50 ± 2 g/L NaCl). The membrane used in this experiment is composed of cellulose triacetate (CTA) and the temperature is set constantly at 23 ± 2 °C. The feed solution is supplied by the active side of the membrane, while the extraction solution is supplied on the side of the shell. During FO experiments, as water diffuses from the feeding solution, the feed becomes more concentrated. As a result of this increase in feed TDS, the driving force and water flow decrease through the FO membrane as the process progresses. The results indicated high water recovery in both brines, with almost 86% and 60% for brine A and B, respectively. On the other hand, the total recoveries of the combined RO-FO system were greater than 96% and 95% for brine A and B, respectively. Recovery was greater in brine A because brine B contained more TDS, which reduced the driving force. Recovery from brine A could have been much higher, but it contained higher concentrations of silica, sulfate, and calcium than brine B, which would cause flakes on the active side of the FO and decrease water flow. Different cleaning methods were used, such as chemical cleaning with Na_2EDTA and osmotic backwash to effectively eliminate embedding.

Similar work has been done on the treatment of brine rejection through the FO technique using a high NaCl extraction solution, where CTA and polyamide (PA) membranes are tested [44]. The concentration of the extraction solution ranges from 35 g/L to 200 g/L, while the concentration of the feed solution ranges from 5 g/L to 15 g/L. Different membrane orientations and their influence on the internal concentrate polarization (ICP) are evaluated. Both the feed water and the extraction solution have been prepared synthetically using sodium chloride and distilled water. The study shows that greater recovery is achieved by increasing the concentration of the extraction solution, which results in the process an increase in osmotic pressure. On the other hand, the driving force decreases when the concentration of the feed solution is increased. Therefore, it is that, when the feed concentration is increased or the extraction concentration is decreased, the permeate flow decreases. Increasing concentrations of extraction and feeding solutions decreases the performance ratio because CP pressure increases. Water flow is affected by the diluent ICP when the feed solution is against the active layer and the concentrated ICP when the feed was placed against the support layer, further decreasing the water flow. Water flows using CTA membrane were 0.0315 L/m²-min to 0.56 L/m²-min, while for the PA membrane a higher water flow range of 0.419 L/m²-min was obtained at 2,785 L/m²-min. This study also indicates that increased cross-flow rate decreases the CP, resulting in a higher flow.

2.1.7 Wind-aided intensified evaporation (WAIV)

One of the most widespread methods for minimizing the volume of brine by thermal means is to use a system called "Wind-Aided Intensified Evaporation" [35]. WAIV technology consists of vertical bed wet towers that use wind energy to evaporate pressed wet surfaces. The WAIV reduces the need for surface area compared to traditional evaporation ponds [43]. For this technique, press-pressure air is sprayed through distribution pipes and transported vertically to the surface of the RO concentrate.

Meanwhile, the serial arrangement of evaporation surfaces with large lateral dimensions leads to optimal use of wind energy, although the air does not become completely saturated with steam. These types of assisted evaporation systems can achieve an evaporation ratio of up to 90% compared to spontaneous evaporation ponds [50].

Using two different desalination brines (RO and RO-ED), it has been estimated that WAIV technology improves the evaporation rate by 10 times more than natural evaporation.

By using WAIV, concentrate TDS can be increased by 23%. Because of this, the possibilities of salt recovery through WAIV and their use as raw materials have been studied [48]. For example, precipitation of less soluble plasters led to enrichment in magnesium salts (magnesium chloride) from RO brine and RO-ED [48]. The membrane crystallizer and WAIV technologies have been integrated to manage the RO concentrate [49].

On the other hand, the recovery factor reached 75% without the presence of an antiscalant and when the pH was low enough that there was no precipitation of calcium carbonate. However, recovery could reach 88% if an antiscalant is applied to the process.

Thanks to this system, the brine discharge is reduced to 0.27 - 0.75% of the total input current to the system [49]. Although the RO concentrate in this study was in the brackish range, the TDS of the concentrate produced by the WAIV system was 78900 mg/L.

In another study on WAIV, it is used to treat RO-ED concentrate in EDR mode [35]. Treatment showed the elimination of approximately 70% of total TDS and was able to recover magnesium salt. Although the RO system with brackish water is also used here, the TDS of the super-concentrated WAIV process was > 30%.

2.1.8 Brine Concentrators (BC)

Brine evaporative cooler/concentrator (BECC) is a thermal technology that was developed to reduce the volume of brine thanks to the evaporative cooling principle. The BECC has two main functions: to cool the recirculating brine and concentrate it for disposal. The outline of the BECC process is shown in Fig. 4 [51].

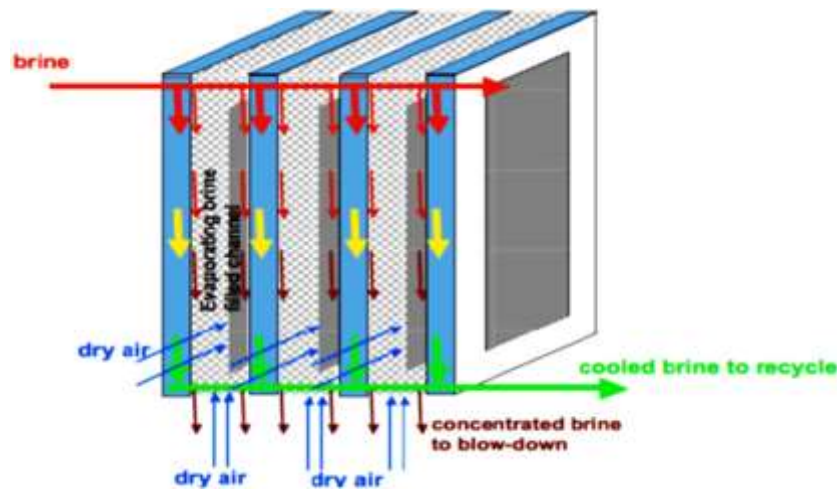


Fig. 5. Brine concentrator functional layout

In the work of Cipollina et al [51], the brine current was cooled in first place, thanks to evaporative cooling, when mixed with a recirculation current (cold sea water) and then concentrated through contact with atmospheric air. A heat-conductive surface separated the two currents and allowed cooling through the recovery of latent heat from evaporation. The results showed that a cooling range of 5 to 10 °C can be achieved with a relative humidity of the air between 40% and 70% and a gas current speed of around 2 m/s. Therefore, it is possible to make cooling and concentration a suitable application for brine rejection management [51, 52].

Some brine concentrators consist of virtual tube through which the concentrate is fed into them [54, 53]. Consequently, the concentrate gets evaporated inside the tube. The concentrate is heated by latent evaporation heat, supplied by the condensation of steam on the outside of the tube, this process produces high purity distilled water, which in turn leads to a decrease in the volume of the final brine. Without scaling, a recovery of 2 to 10% of the steam that would otherwise be discarded can be achieved. In the brine concentrator, there are three limiting factors to consider, these are the elevation of the boiling point of the brine, the relative concentrations of sulfate and chloride and, finally, the

solubility of sodium salts [53]. An overall recovery of 95-99% can be achieved using this system.

2.1.9 Ohmic evaporator

Another thermal process to reduce the volume of the brine produced is the ohmic evaporator. This equipment uses alternating current at a frequency of 60 Hz to evaporate the concentrate of the desalination process in an electric field of 24 – 87 V/cm. This method is only used when the ion concentrations of the brine exceed 80000 ppm, i.e. for very high concentrations. This phenomenon bases its operation on which, the alternating current, when passing through a material with high electrical resistance makes it heat up, increasing the temperature of the medium [55]. The heating produced (ohmic heating) is proportional to the square of the power of the generated electric field and the conductivity of the material.

A good percentage of permeate recovery for this equipment ranges from 81 to 93.5% with an electrical power of 56 V/cm.

However, the economic sustainability of this process remains an issue to be optimized, with numerous research streams dedicated to this topic [56].

2.1.10 Brine crystallizer

Freezing desalination is called a crystallization process. This technique can be carried out through the process of "Eutectic Freeze Crystallization (EFC)", which consists of lowering the temperature of the brine until it reaches the eutectic point for its composition, forming crystals. This equipment is formed by cylindrical vertical containers where thermal exchange is given thanks to steam compressors or, directly, exchangers. This type of equipment is called evaporative crystallizers, in which the primary (and recirculating) concentrate is heated by steam from the compressor in such a way that evaporation of water is caused, but allowing the salts of the concentrate to crystallize [57].

As a rule, evaporation occurs in a shell and tube heat exchanger, applying overpressure to the brine to prevent it from evaporating, and recovering evaporated water for reuse in the plant.

On the other hand, dry solids in this process are usually arranged for a landfill, although, in many cases, crystallized salts can be used at some point in the process or for other applications.

Certain research has used the EFC process to treat hypersaline rejection currents from industrial and mining processes [58]. As a result, it was obtained that the teams working on the eutectic point of dissolution generate drinking water at the same time as the pure salt crystals are produced, in addition, the energy consumed by these is less than the evaporating crystallizers that work without taking into account the eutectic point of the medium. Subsequently, brine from a RO process is used to study this method. The results reveal that 97% of the treated brine flow is recovered as drinking water, in addition, salts such as sodium sulfate or calcium sulfate of 96.4 and 98% purity are also recovered, respectively. The total efficiency of the system considering both the recovered water and the value of the salts obtained is estimated at approximately 99.9%.

EFC is found to be the most vigorously economical alternative to evaporative crystallization, as if the dissolution is cooled beyond the eutectic point, crystals of both salts and ice are produced, losing process performance, even if ice crystals can be recovered and transformed back into clean water.

There are two cooling methods in the industry, direct and indirect cooling, the direct cooling consist of the direct action of the refrigerant within the medium to cool, while in the indirect there is an exchange of heat between the refrigerant and the feed through a contact surface. Although this technology is not exactly modern, it has rarely been done on a large scale, or has been experimented with, this is due to the low productivity of this method [59].

2.1.11 Multi-effect Distillation (MED) and Mechanical Vapor Compression (MVC)

MED consists of a set of tanks in series that perform a distillation process at increasingly less pressures, so that the steam produced in one step is used to heat and evaporate the solution found in the next step and is at lower pressure. This process is used for the treatment of brines from RO. The performance of this process depends to a large extent on the number of steps (or effects) available, in the greater number of steps, the better, although it is estimated that the combination of RO-MED processes can achieve a yield of 93% of the recovered permeate flow. On the other hand, to carry out this process it is necessary the pretreatment of the inlet flow, with the aim of reducing the concentration of silicates and preventing the formation of scaling on the heat exchange surface.

To improve process efficiency, it is common to install a steam compressor between the different steps, in this way, the compressor provides steam energy through a compression process during evaporation, in addition to recirculating it. This combination of techniques is very useful if you want to choose to completely eliminate the discharge of liquids (Zero Liquid Discharge, ZLD).

A mechanical compression of steam can be used to treat brines when it is interesting to obtain distilled water and more concentrated salts [60], the concentrate obtained from this process can be stored and subsequently treated by thickeners and press filters.

As a general rule, this equipment usually operate at a temperature of 80 °C, however, recent studies have shown that operating at 172 °C, lower pressure and less heat transfer area are needed, resulting in smaller equipment size, lower hazards, lower costs [61]. At 172 °C, the salinity of the concentrate is increased by 15%, with a feeding concentration of 35000 mg/L.

2.1.12 Membrane Distillation (MD)

Membrane distillation processes combine two of the most promising fields in brine reduction or removal, membrane separation and heat treatments, an alternative process designed to dehydrate solutions with high salt concentrations. Compared to simple membrane separation, where the driving force was provided by a pressure, concentration, or electrical gradient, the driving force in membrane distillation (MD) is about steam pressure, which is directly related to the temperature differential across the entire membrane surface [42, 62]. Permeate can be produced at temperatures as low as 10 or 20 °C, provided that the differential step between hot and cold currents is maintained [63].

The mechanism of MD operation is based on a liquid-vapor balance where volatile components are diffused through a micro porous and hydrophobic membrane. This system has a high-water recovery capacity from concentrates and can be installed based on various configurations.

The different configurations of an MD system can be direct contact, air bursts, low pressure, and vacuum, although the most widely used system uses direct contact configuration (DCMD). The operation of this configuration is as follows, on one side of the membrane is the flow of concentrate to the highest temperature (of the respective gradient), in this way, the volatile components evaporate and pass through the micropores of the hydrophobic membrane, separating from the liquid phase that does not pass through it and is retained along with the dissolved salts. On the other side, condensation permeate is collected by cooling the steam. Among the advantages of this system are: the vapor pressure gradient, one of the driving forces, is not affected by the concentration of salts carried by the concentrate; low presence of fouling and bio-fouling; the process has the ability to receive heat from the source that best suits the system, solar, geothermal, electrical, etc.; low operating and maintenance costs. On the other hand, the main drawback of this is the low permeate flow obtained in most cases [64].

The performance and sustainability of a membrane distillation system in the recovery of permeate from concentrates from a thermal desalination plant [63] has been investigated in a pilot plant. Three different samples are taken for the pilot plant, Persian Gulf salt water, synthetic saline solutions and, finally, brines from desalination plants, all of which are operating under different operating conditions. In addition, five different types of membranes are used, already marketed and compatible with membrane distillation systems, these membranes are composed of an active layer of polytetrafluorethylene (PTFE) on a polypropylene (PP), supported with different pore sizes and thickness. The temperature range is maintained at 70 and 30 °C for the feed current and distillate, respectively, in addition, it is operated with a flow rate of 1.8 L/min for feeding and distilling.

Under these conditions, a constant permeate flow of 25 L/m²h is achieved using synthetic salt water with a salt concentration of 70000 mg/L. However, if the salt concentration is increased beyond this level, the permeate flow obtained decreases considerably to less than 20 L/m²h.

None of the experiments performed detect fouling, in addition, it is shown that both the permeation flow and the efficiency of the system increase directly proportional to the temperature of the feed current, leaving constant (to maintain the gradient) the temperature of the distillate. All membranes achieve 99.9% of rejected salts in the concentrate flow.

The researchers involved in the experiment recommend the use of the MD system to treat the concentrated rejection of thermal desalination plants, because it is a very efficient system for the production of distillate with very low salt concentration (10 µS/cm conductivity), in addition, because the concentrate of the thermal desalination plants retains some of the heat of the process, this combination is ideal for the recovery of that heat.

On the other hand, a reduction in the rejection flow has also been tested by a distillation system with membranes by direct contact but improved with vacuum (Vacuum-Enhanced Direct Contact Membrane Distillation, VEDCMD) [44]. This system is compared to the direct osmosis process by carrying out a process under the same operating conditions and with the same feed.

The membrane used in VEDCMD is one manufactured from PTFE on a PP support, as explained above, with a pore size of 0.22 µm, a feeding temperature between 40 and 60 °C and a distillate of 20 °C. High permeate recoveries are recorded, reaching up to 81% efficiency from brine concentrates, compared to 96% achieved when dealing with a combination of RO with VEDCMD. It also compares the lowest and highest temperatures recorded for both VEDCMD and FO, and it is shown that VEDCMD has better performance operating at lower temperature for feeds with high salinity and low scaling presence. However, direct osmosis is above VEDCMD when it comes to feedings with high tendency to form scaling and less saline concentration. It is concluded, therefore, that a scaling inhibitory treatment is convenient in processes to improve the performance of VEDCMD.

On the other hand, experiments have also been conducted with a Vacuum Membrane Distillation system (VMD), yielding interesting results [65]. In this test, brines of synthetic production with high saline concentrations (up to 300,000 mg/L) are tested under different operating conditions. The results shown by this process indicate that high percentages of permeate recovery can be achieved, even if there are high saline concentrations in the feed by using a highly permeable membrane, a low permeate collection pressure and, finally, raising the temperature of the feed current as much as possible. The permeate flow obtained varies between 7 and 19 L/m²h when the feed salt concentration is between 64,000 and 300,000 mg/L at 50°C and 6 kPa of pressure in the permeate. In addition, it is demonstrated that scaling is only presented when working with high salinity feeds, which may be due to the presence of low solubility compounds that precipitate in the solution, such as sulfate or calcium carbonate, yet this event is reversible and the formed crystals can simply be collected and removed when the membrane is being cleaned with clean

water. It is concluded that, for the treatment of brines from RO with a VMD system, a high recovery of permeate, up to 89%, can be achieved, minimizing the volume of brine considerably.

Among other processes that use membrane distillation technology, the system of air bursts in a multistage membrane distillation (AGMD) and using hollow fiber membranes, is widely used to achieve high permeate ratios from the brine rejection of RO processes [66]. In this way, it is observed that the performance of the process increases as the number of stages rises, being 5 to 8% recovery for systems with one stage, and up to 22.2 or 24.7% recovery when 4 is available. The maximum recovery percentage is found when using a system with 14 stages, where you get an 88.2% recovery of permeate with a concentration in the feed of 352,000 mg/L. Thanks to all this data, it is concluded that the AGMD system can be used to treat currents with high saline concentrations.

2.2 Direct removal of brines

A conventional approach in the brine treatment is the direct disposal to large water bodies like seas, oceans, etc. or injection into inland wells [67]. However, this kind of solution has the worst consequences to marine environment and underground water due to, as indicated by “P. Oceánica” [68], the elimination of reject brine with high salinity could affect to different kind of marine species, the high temperature of the reject current also negatively affects to the surrounding areas decreasing the concentration of dissolved oxygen in water and, therefore, helping to create a hypoxic environment, which harms all living beings who inhabit it. In addition, there is a risk of leaks with high salinity concentrations when the disposal of the brine is being produced to the underground wells, which can gravely affect the terrestrial environment [69]. Therefore, the direct disposal method is not recommended unless it is the only feasible alternative.

The direct disposal of the rejected brine into large bodies of water have been practiced since past years by several countries. In order to carry out this procedure, the discharge must be very diluted to the legal level determined by the properties of the discharge current itself and the characteristics of the receiving aquatic environment. The concentrate properties are defined by the TDS, the density and the discharge flow, on the other hand, the environment properties where this current is rejected are determined by physical characteristics such as the volume of the water body and the biological content of the surrounding area. Different factors such as the location of the underwater emissary, extent of mixing and the water currents capacity to transport the mixed brine must be studied in order to realize the direct discharge of the reject brine into any sea. Due to the high salinity content in the reject current in comparison with the sea water, there is a possibility that the current sinks and be diluted into the bottom of the ocean, as it is much denser. Although the most common result in most cases is horizontal spreading [70]. To solve this situation, an alternative method is proposed to avoid the direct discharge of rejected brine into the seas [71]. The conventional method requires a discharge angle of 60° to the horizontal but, however, extent of dilution when the sea is at maximum sea rise is not provided with this angle. In addition, it is shown that an angle of 30 or 45° to the horizontal can seriously improve the operation design. Some of these benefits are a better degree of dilution, better brine dilution when sea currents are weak and the possibility of placing the underwater emissary in shallow places or near the coast to cost reduction [71].

Normally, a plume develops on the sea surface due to the large difference in concentrations between the rejected brine and the pouring medium. This generates negative environmental effects, so have been studied the best way to achieve the optimized disperse of the plume [72]. First, this plume is considered to come from the rejected brine of a desalination plant in the Persian Gulf, dilution through multiple outlets is shown as the most feasible method to improve mixing, eliminate the plume and reduce environmental impacts.

Another studied option consists in the mixing of brine concentrate with sewage before it is discharged into the sea, which decreases the salinity of the concentrate. Sometimes, there are systems to inject brine concentrate directly into the sewer, which causes it to mix naturally with wastewater, producing a single effluent of lower salinity and temperature, however, there is a possibility that treatment of this mixture is necessary before it is discharged into the environment, which only depends on the characteristics of the wastewater flow, as the retention capacity of organic compounds in the brine concentrate flow may cause the flow mixture to not be safely discharged at sea [73]. In addition, the high salinity of the concentrate can cause wastewater to be treated under certain conditions [74]. Due to all these factors, brine rejection has been attempted to mix with cooling water from power plants rather than wastewater, which is possible as long as the plant in question is located near the desalination facilities. This technique seems quite feasible because both currents are compatible, so that a cold and dense stream of concentrate is being mixed with another hot and light cooling water. As a result of this mixture, the time required for dilution at sea is reduced, increasing the degree of dilution of the discharge.

Another way of removing the brine concentrate is the grounding technique, which is an economically viable option for desalination plants that are placed far from the coast. Injection into deep groundwater reserves is a method of elimination by which rejected brine is injected into an underground aquifer containing non-drinking water, however, this system could create uncertainty about the environmental impact by being very complex measuring it [76, 75]. Deep well injection is an advanced disposal technique used worldwide. Some of the most important factors to consider for a good discharge are the geological strata, the desired underground aquifer depth, the type of well used, the availability of the well, the compatibility between the well water and the brine and the possible reception that this may have for the population [77]. A porous injection site able to withstand the injection flow rates during the installation life is required. In addition, a geological layer of hydrophobic materials, such as clay or mother rock, is required to prevent leakage into freshwater streams or terrestrial environment of the injected brine [76, 75]. Another alternative under study is the injection of brine concentrate into a depleted oil well, which is feasible to improve the reduced pressure normally resulting from oil wells after constant production [78]. Six wells were studied for brine injection recovery research, with different rates of oil production recorded as a result of injection. It is therefore concluded that brine injection into low-level oil wells is a viable form of pressure recovery approach for all wells [78].

Studies such as Badescu et al [79] have developed different ways of enhancing the sustainability the brine removal through submerged pipes. Technical, economical, and environmental restrictions are defined in order to discover the best way of brine removal, with the aim of reducing the energy spent with this method. Among other aspects, the optimal pipe length and depth of the discharge point are determined. In the study of Schuiling et al [80] the brine removal from Strait of Ormuz to the Arabic Sea without any energy expenditure is examined.

2.3. Reuse application of reject brine

Despite the fact that some processes may be effective in recovering and minimizing the volume of brines, it should be considered that this current can be a valuable resource for the production of mineral salts, metals and/or chemicals. Currently, different technologies are focused on the production of salt and chemicals from brine to ensure the reduction of the total cost of the desalination process. In addition to the economic benefits, rejected brine recovery can reduce the environmental impacts associated with this process [81, 82]. However, the capital and operating costs of these systems are obviously higher than those associated with a common desalination process with no brine recovery at all. There is a wide range of research to recover salts from the residual brine to use reuse them for other applications [81 - 88], this idea is explained more extensively below.

2.3.1. Chemical precipitation

Chemical precipitation is a feasible method for recovering salt from rejected brine. This method has been carried out by using various precipitating agents [85]. As an experiment for salt recovery, different samples such as untreated seawater, synthetic seawater and two concentrates of reverse osmosis processes obtained from desalination plants located around the Mediterranean and Red Sea coasts were used, sodium phosphate and sodium carbonate were used as chemical precipitants. Magnesium and calcium salts were recovered thanks to the precipitating agents used. Using sodium phosphate, calcium recovery was 98% and 75% from seawater and RO concentrate, respectively, 47% and 24% of magnesium recovered from seawater and RO concentrate, respectively as well.

Using sodium carbonate to achieve precipitation, calcium reduction was achieved from 690 mg/L to 36 mg/L and 400 mg/L to 20 mg/L for RO concentrate and seawater, respectively. In addition, magnesium concentration decreased from 2600 mg/L to 2375 mg/L and 1460 mg/L to 1250 mg/L for RO concentrate and seawater, respectively. Per kg of sodium carbonate used, 2 kg/m³ of tracing and magnesium deposits were obtained from the RO concentrate. In addition, 1.43 kg/m³ of seawater tanks were obtained. Prior to chemical precipitation, pretreated with membrane/thermal and ion exchange technology were carried out to improve the obtained results. This technology is suitable for new plants, or to modernize current desalination plants with nanofiltration membranes in such a way that brine obtained with this method can be treated with a two-stage chemical treatment and an ion exchange purification. Rejected brine can also be decalcified in such a way that ion exchange can be used to remove magnesium from the decalcified current. In order to implement these changes at the industrial level, the optimization and economic analysis of these treatments are a priority.

The valorization of calcium and magnesium subproducts of concentrated RO brine through chemical precipitation using sodium carbonate precipitants and sodium hydroxide at 25°C and 65°C is another salt recovery technique [89]. Casas et al. [89] observed that calcium removal was affected by temperatures above 65°C, but magnesium removal was not affected. In addition, calcium and magnesium recovery was masked by antifouling agents and metal ions present in the rejection current; therefore, it was necessary to concentrate even more the rejected brine by using electro dialysis systems, which helps reducing the amount of antifouling agents. 0.35-14 g/L sodium carbonate and 0.85 g/L sodium hydroxide were used to achieve the greatest calcium and magnesium removal. 10 mg/L of calcium and magnesium remained in the residue of the ED-RO process and elimination efficiencies of >95% were achieved in all experiments. The order of treatment processes did not influence overall disposal efficiency. Although low concentrations of calcium and magnesium were observed in residual subproducts, they may not be suitable for some applications because they still contain NaCl. Meanwhile, these subproducts can still be used as agents to control pH and recover fertilizers containing wastewater treatment phosphates.

2.3.2. Adsorption

The rejection of brines from desalination processes is a potential source of metal collection. A simple and effective way to get those metals can be through an adsorption process. Although the following properties of the metals must be taken into account in determining the metal to be recovered from rejected brines: physical properties, chemical characteristics, technical feasibility of the use of adsorbents to remove metals from the brine resource and economic and environmental benefits derived from the recovery of such metals [90, 91]. The feasibility of using various adsorbents to recover metals such as rubidium, cesium, uranium and lithium from seawater RO brine [90] has been investigated. It was concluded that the hexacyanoferrate-based extracting medium (CsTreat) was the best adsorbent for cesium and rubidium extraction. Cesium

extraction using CsTreat was not significantly influenced by salinity. In addition, CsTreat was able to select only cesium and rubidium for adsorption. However, different results were obtained for adsorption in metallic and bimetallic systems, performing worse in bimetallic systems. Lithium could not be eliminated by any adsorbent and remained in the brine.

In addition to the associated environmental benefits, high returns on investment in metal recovery from brine rejection can be obtained, especially for uranium, a very valuable material as an energy source through nuclear energy. However, metal recovery technologies require more research in order to improve the extraction process and the performance in near future [92]. A similar investigation has evaluated the extraction of valuable metal ions from the RO concentrate using selective sorbents [93]. Cesium, lithium, rubidium and uranium have been included in the group of metal ions. These metal ions (Cs(I), Li(I), Rb(I) and U(I)) were extracted using commercial sorbents, namely CsTreat, ZrP and S910. It was reported that CsTreat was able to achieve the highest extraction capacity for Rb(I) and a reasonably high adsorption of Cs(I). S910 had a good adsorption capacity for U(VI) but that of Li(I) by ZrP was unsuccessful. It was determined that there is a need for further research and studies aimed at recovering valuable metals from residual brine using different adsorbent agents and adsorbent-based materials in order to achieve an economically feasible and a technically simple method [93].

An adsorbent resin (chelating resin crosslinked polymer resin) has been developed and experimentally characterized in discontinuous fixed-bed column operation to select and extract uranium from brine [94]. The polymer chain has stereoselectivity towards the widely populated tricarbonyl complexes in uranyl compounds that may be present in some concentrated solutions. This is especially important when the source of concentrate is residual brine of RO, which normally has a mild acid pH and contains a lean amount of target uranium. In addition, there is competition between the uranium complex and other ions present in the brine to occupy the resin. This resin was characterized by a remnant of hydroxyamic acid because it was discovered that the acid achieved an adequate selectivity, good adsorption speed, adequate mechanical resistance, good load resistance, simple elution and detection by chromatographic means in such a way that it can be altered by polymers of different sizes and shapes. This process was shown to exhibit better economic viability, but it was concluded that more research is needed to make the extraction process more efficient by reducing the steps involved, which will eventually reduce the cost of treatment.

Another study used BAMBP [4-tercbutyl-2-(a-methylbencil) phenol] or 4-sec-butyl-2-(a-methylbencil) phenol] to extract the rejected brine rubidium obtained from a RO desalination plant with a capacity of 100,000 m³/d [91]. More than 80% rubidium was recovered. NaCl was also extracted from the rejected brine. In the same way, an attempt was made to extract phosphorus with the extractor agent, but this step was not economically feasible. This can be achieved on an industrial scale if restrictions on phosphorus discharge are increased. The extraction of phosphorus from the rejected brine would result in significant environmental advantages because it would reduce eutrophication in the natural environment.

2.3.3. Membrane and electrokinetic processes

The behavior of nanofiltration for the removal of sulfates and chlorides from brine [95] has been tested in pilot-scale experiments. Experimental results were theoretically compared to the Donnan Steric Pore Model (DSPM). The membrane used for the process (NF270) provided good results with a sulfate rejection of 70-96% and a chloride rejection of 2-11% under an operating pressure of 500-2000 kPa, an ion force of 0.1-1.3 M and an initial chloride concentration of 0.2-1.2 M. Through the mathematical model an accurate description of the experimental ion rejection of the membrane was obtained using the pore radius, the thickness of the membrane layer and the load density of the membrane. This study concluded that the nanofiltration separation process to

remove sulfate and chloride was effective for highly concentrated saline solutions and efficiency of the process could be predicted through the use of the mathematical model used.

Bipolar membrane electro dialysis (BMED) has also been applied to reuse RO rejection brine generated from a seawater desalination plant, turning it into products with both possibilities, acidic and basic pHs [96]. It was shown that it is possible to produce acids or bases with concentrations of 1 M or higher with an efficiency of between 60 and 90 % thanks to this process. On the other hand, efficiency is affected by the transfer of ions to the highest concentration of acid through the anionic exchange membrane as opposed to the slow movement of the co-ions and to the most basic parts through the membrane. The inlays and scales of the membrane were caused by multivalent anions and cations; therefore, it was recommended a pretreatment prior to the principal treatment with BMED. The acid and base produced by this method include hydrochloric acid and sodium hydroxide [96].

Sodium hypochlorite can be generated through on-site electrochlorination from brine residues [97]. An electrolysis cell can be used for the process by feeding brine and exposing it to a minimum voltage of direct current (DC). In the work of Abdul-Wahab and Al-Weshahi [97], sodium hypochlorite appears instantly as the electrolyte process took place. This method prevents hazardous chlorine gases and the risks of transporting it since the production occurs in the form of sodium hypochlorite. These benefits improve the process environmentally. In addition, hydrogen gas could also be produced and transported through a pneumatic transport system [97]. Because hypochlorite is preferred over chlorine as an anti-incrustant and disinfectant, the cost of purchasing hypochlorite for the main desalination process can be saved by recycling hypochlorite from treating the same brine. This method can be a solution for brine waste management and a business opportunity to environmentally improve the desalination process, making it more sustainable.

The separation of brine salts by electro dialysis is improved by the use of cationic and anionic exchange membranes located between the electrodes and connected to the electrical current. This process can be used as a pretreatment step before other methods, such as evaporative cooling or crystallization, so that brine can be dehydrated first. This step is also necessary to remove calcium or sulfate ions that may cause gypsum crystallization [82, 83]. Inlays due to organic and colloidal particles should be considered when designing electro dialysis cell to remove salt from rejected brine [82]. This mechanism has also been used to study the possibility of water recovery, in addition to the salts recovery [84]. This process consists of four anionic exchange membranes and five cationic membranes. The performance impact of variation on operating conditions, such as membrane characteristics, current density, and initial brine concentration, was investigated. It was observed that the electro-osmotic potential influenced the displacement of water from the saline solution, leading to a recovery of 67.78% fresh water and a desalination rate of 72.74%. In addition, a highly concentrated output brine was obtained, reaching 27.13% m/V, and can be used for the production of edible sea salt by crystallization.

2.3.4. Crystallization and evaporation

One approach to salt recovery from brines is Selective Salt Recovery (SSR) by crystallization. SSR could also be called fractional crystallization, as it involves precipitation of dissolved salts through alterations in the concentrations of these, through the influence of temperature changes. The SSR involves a sequence of processes designed to recover specific salts from concentrates based on differences in their solubility and their ease of being precipitated or adsorbed [98, 99, 88]. The marketing of salts produced from SSR makes this approach cost-effective and beneficial to the environment, since instead of discharging these salts to the environment they are recovered for commercial applications. The performance of the SSR process is influenced by operating conditions, such as pressure, pH and other components, in addition to the characteristics of the salts to be obtained. The wide variety of forms of saline particles and their ability to remain in an

unstable balance (metastability) are key factors in the kinetics of the process and must be studied before choosing any operating conditions for SSR. Selective salt precipitation is particularly influenced by process pH, temperature, residence time, the presence of antifouling agents, mixing efficiency and the physicochemical nature of salts in terms of crystal shape, size, and purity [98, 99].

Currently, the use of the SAL-PROC™ system and brine concentrators are the most common steps in a SSR process [88]. The most important salts are those that are cost-effective, such as gypsum, calcium carbonate, magnesium hydroxide, sodium sulfate, sodium, and calcium chlorides. These can be recovered from salt water by selective extraction using the SAL-PROC process™ [88]. This approach requires some sequential steps of chemical processing and evaporation cooling. Theoretically, the salt recovery obtained from the process was the 100% and the ZLD of the rejected brine can be achieved with this method [92, 99, 81, 88]. One point of improvement to consider with respect to the SSR process is the optimization of salt production for human consumption, which guarantees greater respect for the environment due to the reduction of brine discharges and a higher profitability of the desalination process [99].

Mineral salts can also be segregated from brine using evaporation or distillation technologies [92, 87]. In addition, the thermal energy required for these technologies can be supplied by renewable energy production sources, such as solar energy. The RO concentrate of a brackish water desalination plant has been used to produce salts with the help of a solar pond [87]. The plant produced about 12,024 m³ of rejection. Before salt recovery, salt forms were produced in liquid, crystalline and solid suspension states thanks to the solar pond. These salts contained K⁺, Na⁺, Ca²⁺, Mg²⁺, SO₄ and Cl₂. Research was conducted using potentiometry, gravimetry, SEM and XRD analysis to analyze these components, demonstrating that the evaporation of the concentrate at a certain temperature and pressure can be used to recover certain salts, including potassium chloride, sodium chloride, magnesium sulfate heptahydrate, and calcium sulfate dehydrated. Salts are important for agricultural and industrial applications [81]. Solar evaporation ponds can also be combined with other brine management practices to produce energy or salts. Salts produced from this type of processes include potassium chloride, potassium sulfate, sodium sulfate, lithium sulfate and boric acid [100].

Another approach to thermally segregating water and salts from the saline solution is the use of a heat pump [82]. Using isothermal evaporation, one study investigated the recovery of mineral salts present in the rejection brine of an RO process that operated with seawater and reported that calcium, magnesium and silicon were first eliminated by a pretreatment with soda lime [101]. The volume of the concentrate was subsequently reduced by evaporation and, at the same time, profitable salts such as sodium sulfate were produced. It is established by the results obtained that 81-88% of Na₂SO₄ was contained in the by-products of sodium sulfate. Only 1% of the original brine volume remained after evaporation. In addition, the complete extraction of Na₂SO₄ was achieved. Although the total cost of desalination can be reduced by recovering salts through this method, additional economic analysis is required to study the economic viability of this approach on a long-term and industrial scale.

2.3.5. Regeneration of wetlands and agriculture applications

Rejection brine can be used to regenerate wetlands and salty ecosystems that suffer from progressive degradation due to drought and human action. These wetlands can be useful for agricultural, livestock, industrial, and local fauna and flora development. Two possible variants of regeneration processes are noteworthy: the regeneration of both coastal and continental wetlands. In the regeneration of coastal wetlands, brine from a seawater-based desalination process should be used, while, in the regeneration of continental wetlands, brine must come from RO processes working with brackish water. The economic and environmental effects of this approach depend on the used brine and the characteristics of the wetland being restored. Working

with this method would with no doubt improve the quality and availability of water resources [102, 82, 103, 104]. Rejection brine can be used for the cultivation or irrigation of a diverse number of species such as plants, animals or microorganisms that are tolerant to slightly higher saline concentrations than freshwater or than seawater. Two of the most studied options are the cultivation of Artemias (brine shrimp) and the *dunaliella* saline microalgae [102, 105]. Artemia is a small crustacean that is no more than two centimeters long and only appears in high salinity waters (70 g/L to 340 g/L), although it can also develop in seawater. It is used as a natural food for larvae or young and adult species of fish and shellfish [102]. On the other hand, *Dunaliella salina* is a microalgae chlorophyte that stores large amounts of carotenoids (up to 14% of its dry mass) and contains high amounts of glycerol, which makes it a natural source of carotenoids. In addition, it generates products that are useful for pharmaceutical or food applications [106]. Research by Raja et al. [106] has shown that higher rates of carotenoid production can be achieved using this method compared to commonly used crop techniques. Although the mechanism in which brine stimulates the production of carotenoids in *Dunaliellas* has not yet been described, it opens up the possibility of using this type of crop as an alternative, especially in areas where there is a high presence of brine from desalination processes due to lack of fresh water [102, 106].

In addition to the previous mentioned, algae farming in ponds in natural brine conditions has also been investigated in a pilot-scale unit [107]. The unit consisted of three parallel rafts for open spaces in natural conditions. *Scenedesmus* algae were grown in laboratory in controlled media to optimize their growth in saline water, after this process, they were introduced into rafts, which contained water with a salinity range of 40,000-80,000 mg/L under constants measurements in order to obtain the efficiency in the removal of Dissolved Total Solids (DTS). The results showed that the DTS elimination efficiency of algae species varied in a range of 13% and 63% [107]. The variation in disposal efficiency was due to the concentration of DTS, the retention time on the raft, and the conditions. This method was considered to have achieved high DTS elimination and the highest final concentration was at permissible limits for safe injection into the sea.

An additional option is to use the brine to grow fish species that are able to live in saline environments. Finally plants species that are tolerant to high salinity levels or brackish water (up to 8000 mg/L) such as beetroot, sugar cane, cotton, dates, barley, spinach, asparagus, or wheat can be grown using reject brine [102]. Some grasses nowadays such as *Paspalum* can also be irrigated with high salinity water. However, additional research works are still needed to evaluate the ability of biological cells to grow in brine with or without pretreatment and the environmental cum economic implications of this type of application.

3. BRINE CONCENTRATION

This part of the Project has been studied due to the “Turbomachinery conference and exhibition” which took place in Sevilla, in June of this same year (2020). Many interesting projects were presented in this exhibition, but it is one of them that is especially striking and causes the inclusion of these calculations in the work. This simulation is reflected in an article called "Micro Gas Turbines Supporting Renewable Energy Systems in Off-Grid Water Treatment Facilities in the Mining Industry", which introduces the outlet gases from a microturbine system to help heat salt water, causing its evaporation and thus obtaining water with higher concentration in salts, and evaporated water of higher purity level. In this way, the residual heat of these gases can be used at a relatively low temperature to obtain a considerable source of drinking water.

This section details the calculations and equations for a saltwater concentration system heated with flue gases, adapting the article system to project-specific operating conditions. The system is as follows:

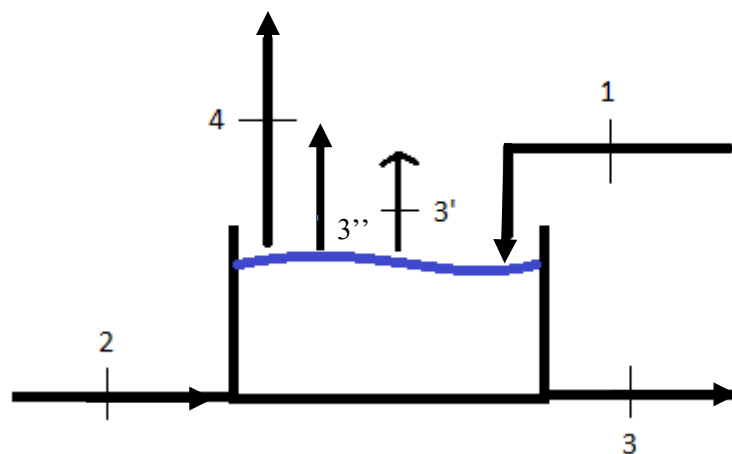


Fig. 6. System diagram

Siendo:

- **Current 1:** input of pre-heated brine.
- **Current 2:** gases input.
- **Current 3:** brine outlet flow already concentrated.
- **Current 3':** water loss due to evaporation due to the heat incorporated by gases.
- **Current 3'':** water losses from drag due to gas speed. In distillation plants, the gases formed pass through a dehumidifying mesh, referred to as demister, that retains moisture droplets. For this particular case and due to the large flow rates that are handled, calculations for drag losses are considered negligible.
- **Current 4:** outlet of cold gases.

It is detailed a matter and energy balance to define the system.

3.1. Matter balance

$$\dot{m}_2 = \dot{m}_4 \quad [1]$$

$$\dot{m}_1 = \dot{m}_3 + \dot{m}_{3'} \quad [2]$$

$$\dot{m}_1 \cdot S_1 = \dot{m}_3 \cdot S_3 \quad [3]$$

$$\dot{m}_1 = \dot{m}_{S1} + \dot{m}_{w1} \quad [4]$$

$$\dot{m}_3 = \dot{m}_{S3} + \dot{m}_{w3} \quad [5]$$

$$S_1 = \frac{\dot{m}_{S1}}{\dot{m}_{S1} + \dot{m}_{w1}} \quad [6]$$

$$S_3 = \frac{\dot{m}_{S3}}{\dot{m}_{S3} + \dot{m}_{w3}} \quad [7]$$

$$\dot{m}_{S3} = \dot{m}_{S1} \quad [8]$$

Where:

$\dot{m}_1, \dot{m}_2, \dot{m}_3, \dot{m}_4$: are the mass flow rates of their respective currents. As operating conditions, it is based on a known flow rate for currents 1 and 2.

S_1 y S_3 : it shows the saline concentration of currents 1 and 3 in kg of salts per kg of flow.

$\dot{m}_{3'}$: is the flow of evaporated water. This loss of water is the cause of the concentration reflected in the current output (3).

\dot{m}_{S1} y \dot{m}_{S3} : these are the salt flow in currents 1 and 3. The difference between flows in current 1 and 3 is the amount of water loss by evaporation.

$\dot{m}_{w1}, \dot{m}_{w3}$ y $\dot{m}_{w3'}$: it shows the water flow in the currents 1, 3 and 3'.

3.2. Energy balance

In this case, in order not to complicate the calculations too much, it is considered an adiabatic heat exchange system with water evaporation. Thus, the system remains:

$$\dot{Q} = \dot{m}_2 \cdot (h_2 - h_4) \quad [9]$$

$$\dot{Q} = \dot{m}_3 \cdot h_{sw3} + \dot{m}_{3'} \cdot h_{aev} - \dot{m}_1 \cdot h_{sw1} \quad [10]$$

$$h_{sw3} = h_{w3} - S_3(a_1 + a_2 \cdot S_3 + a_3 \cdot S_3^2 + a_4 \cdot S_3^3 + a_5 \cdot t_3 + a_6 \cdot t_3^2 + a_7 \cdot t_3^3 + a_8 \cdot S_3 \cdot t_3 + a_9 \cdot S_3^2 \cdot t_3 + a_{10} \cdot S_3 \cdot t_3^2) \quad (J/kg \cdot K) \quad [11]$$

$$h_{sw1} = h_{w1} - S_1(a_1 + a_2 \cdot S_1 + a_3 \cdot S_1^2 + a_4 \cdot S_1^3 + a_5 \cdot t_1 + a_6 \cdot t_1^2 + a_7 \cdot t_1^3 + a_8 \cdot S_1 \cdot t_1 + a_9 \cdot S_1^2 \cdot t_1 + a_{10} \cdot S_1 \cdot t_1^2) \quad (J/kg \cdot K) \quad [12]$$

$$h_{w1} = 141,355 + 4202,07 \cdot t_1 - 0,535 \cdot t_1^2 + 0,004 \cdot t_1^3 \quad (J/kg) \quad [13]$$

$$h_{w3} = 141,355 + 4202,07 \cdot t_3 - 0,535 \cdot t_3^2 + 0,004 \cdot t_3^3 \quad (J/kg) \quad [14]$$

$$h_{evw} = 2,501 \cdot 10^6 - 2,369 \cdot 10^3 \cdot t_x + 2,678 \cdot 10^{-1} \cdot t_x^2 - 8,103 \cdot 10^{-3} \cdot t_x^3 - 2,079 \cdot 10^{-5} \cdot t_x^4 \quad (J/kg) \quad [15]$$

$$t_x = t_3 + BPE \quad [16]$$

$$BPE = X(B + C \cdot X) \cdot 10^{-3} \quad [17]$$

$$B = (6,71 + 6,34 \cdot 10^{-2} \cdot T + 9,42 \cdot 10^{-5} \cdot T^2) \cdot 10^{-3} \quad [18]$$

$$C = (22,238 + 9,59 \cdot 10^{-3} \cdot T + 9,42 \cdot 10^{-5} \cdot T^2) \cdot 10^{-8} \quad [19]$$

The equations from [16] to [19] are referenced by [111].

After that, it is shown the enthalpy variation equations for the combustion gases:

$$h_2 - h_4 = \Delta h_{gases} = \int_{T_2}^{T_4} C_{pm}(T, p \rightarrow 0) dT + \left[\left[B(T_2) - T_2 \cdot \frac{dB(T_2)}{dT} \right] \cdot p_2 - \left[B(T_4) - T_4 \cdot \frac{dB(T_4)}{dT} \right] \cdot p_4 \right] \quad [20]$$

Where the equation to get the Cp and the second virial (B) is:

$$C_{p,m}(T, p \rightarrow 0) = [27,659 + 4,47 \cdot 10^{-3} \cdot T(K)] \quad (J/mol \cdot K) \quad [21]$$

$$B(T) = \left[126,301 - 87,127 \cdot e^{\frac{129,104}{T}} \right] \cdot 10^{-6} \quad (m^3/mol) \quad [22]$$

Knowing all this data, the formula for calculating it is:

$$\Delta h_{gases} = \frac{10^3}{28,965} \cdot \left[\left[27,659 \cdot (T_2 - T_4) + \frac{4,470 \cdot 10^{-3}}{2} \cdot (T_2^2 - T_4^2) \right] + \left[\left(126,301 - 87,127 \cdot e^{\frac{129,104}{T_2}} + 87,127 \cdot \frac{129,104}{T_2} \cdot e^{\frac{129,104}{T_2}} \right) \cdot p_2 \cdot 10^{-6} \right] - \left[\left(126,301 - 87,127 \cdot e^{\frac{129,104}{T_4}} + 87,127 \cdot \frac{129,104}{T_4} \cdot e^{\frac{129,104}{T_4}} \right) \cdot p_4 \cdot 10^{-6} \right] \right] \quad (J/kg) \quad [23]$$

Where:

\dot{Q} : it is the thermal heat provided by the outlet gases of the microturbine.

T_2, T_4, T_3, T_1 : these are the temperature of their respective currents.

h_{sw1}, h_{sw3} : these are the enthalpy regarding the state of reference (Sharaqawy, 2010) [110], based on salinity and temperature, the effect of the pressure is negligible in this problem.

h_{wT1} y h_{wT3} : these are the enthalpies of pure water at the temperatures of the current 1 and 3, respectively.

h_{aev} : it is the water vaporization enthalpy, assuming thermodynamic balance whit current 3. It is obtained from the enthalpy vaporization of pure water and salinity of a flow, in Sharqawy (2010) [110].

h_{evw} : it is the vaporization enthalpy of pure water.

h_2, h_4 : these are the input and output enthalpies of the combustion gases, respectively. These gases are considered dry when entering the system.

a_i : These are constants from Sharqawy (2010) [110]:

$$a_1 = -2,348 \cdot 10^4$$

$$a_2 = 3,152 \cdot 10^5$$

$$a_3 = 2,803 \cdot 10^6$$

$$a_4 = -1,446 \cdot 10^7$$

$$a_5 = 7,826 \cdot 10^3$$

$$a_6 = -4,417 \cdot 10^1$$

$$a_7 = 2,139 \cdot 10^{-1}$$

$$a_8 = -1,991 \cdot 10^4$$

$$a_9 = 2,778 \cdot 10^4$$

$$a_{10} = 9,728 \cdot 10^1$$

t_i : temperature of the current i , expressed in °C.

3.3. Each current data

Below are the data from which they are based for each current:

- **Current 1:**

$$T_1 \in [60,100] \text{ } ^\circ\text{C} ; P = 1 \text{ atm}$$

$$S_1 \in [0.07,0.085] \text{ kg/kg}$$

Other necessary data such as specific heat or pure water evaporation enthalpy at the temperature of this current are called from the software used for testing this system.

- **Current 2:**

$$T_2 \in [225, 325] \text{ } ^\circ\text{C} ; P = 1 \text{ atm}$$

There are supposed dry gases and an adiabatic system.

The specific heat and the enthalpy of this current is calculated using the equations shown in the thermodynamic notes from Carlos Gómez (2012-13) [[109](#)].

- **Current 3:**

$$T_3 = 102 \text{ } ^\circ\text{C}; P = 1 \text{ atm}$$

Same conditions as in the current 1.

- **Current 4:**

$$T_4 = 120 \text{ } ^\circ\text{C}; P = 1 \text{ atm}$$

Its flow rate is the same as the gas inlet.

- **System degrees of freedom**

Inlet of saltwater flow temperature [60, 100] °C.

Temperature of the input combustion gases [225, 325] °C.

The optimization searched with this work lies in the mass flow of the concentrated brine current (m_3) and its salinity (S_3).

4. CONCLUSIONS

Previous equations from part 3 are introduced in the software “Matlab”, simulating the system under the conditions specified in this part. The conclusions obtained studying this problem are exposed below.

4.1. Effect of T_1 y T_2 in the mass flow m_3

Figure 7 shows the behavior of the oversized flow of the brine current to the output versus the evolution of the temperatures of the combustion gases and brine at the inlet of the control volume.

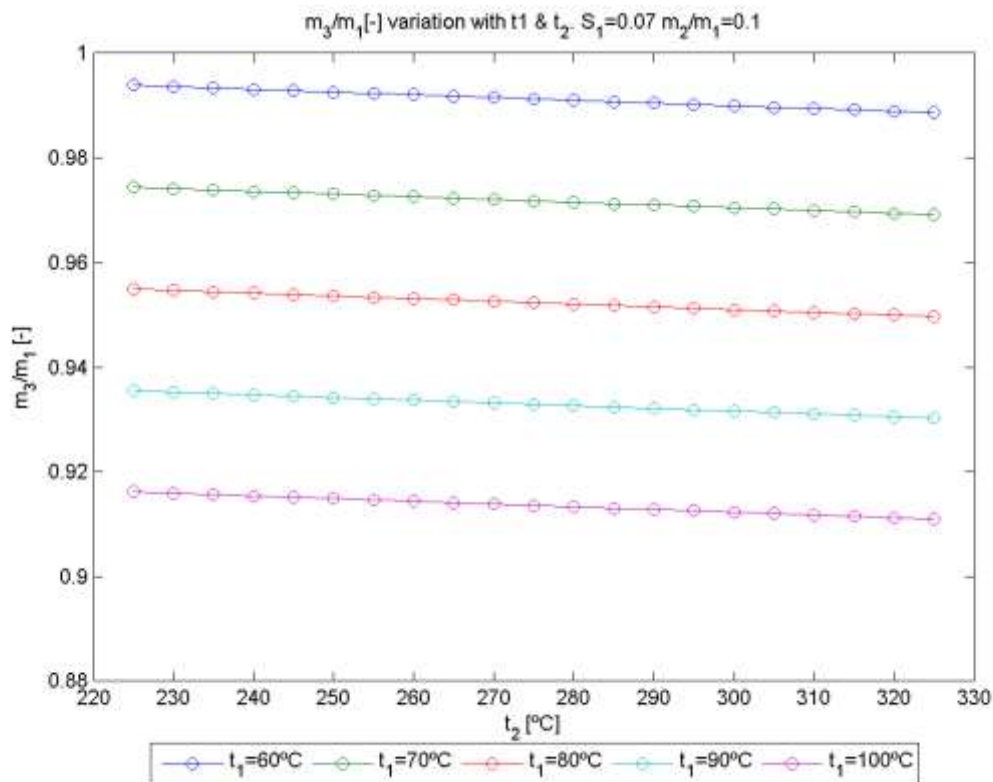


Fig. 7. m_3/m_1 tendency with T_1 , T_2 variations

The mass flow of the concentrated brine current (m_3) must be less than the inlet flow (m_1) due to evaporation losses. And therefore, trends in both T_1 and T_2 are similar, is any of them increase them the evaporation does, so therefore decrease m_3 . Being therefore the ratio of $m_3/m_1 < 1$ and decreasing with the increase of both temperatures.

4.2. Effect of T_1 y T_2 in the salinity S_3

Figure 8 shows the salinity behavior of the brine current (S_3/S_1), versus the evolution of the temperatures of the combustion gases and brine at the inlet of the control volume.

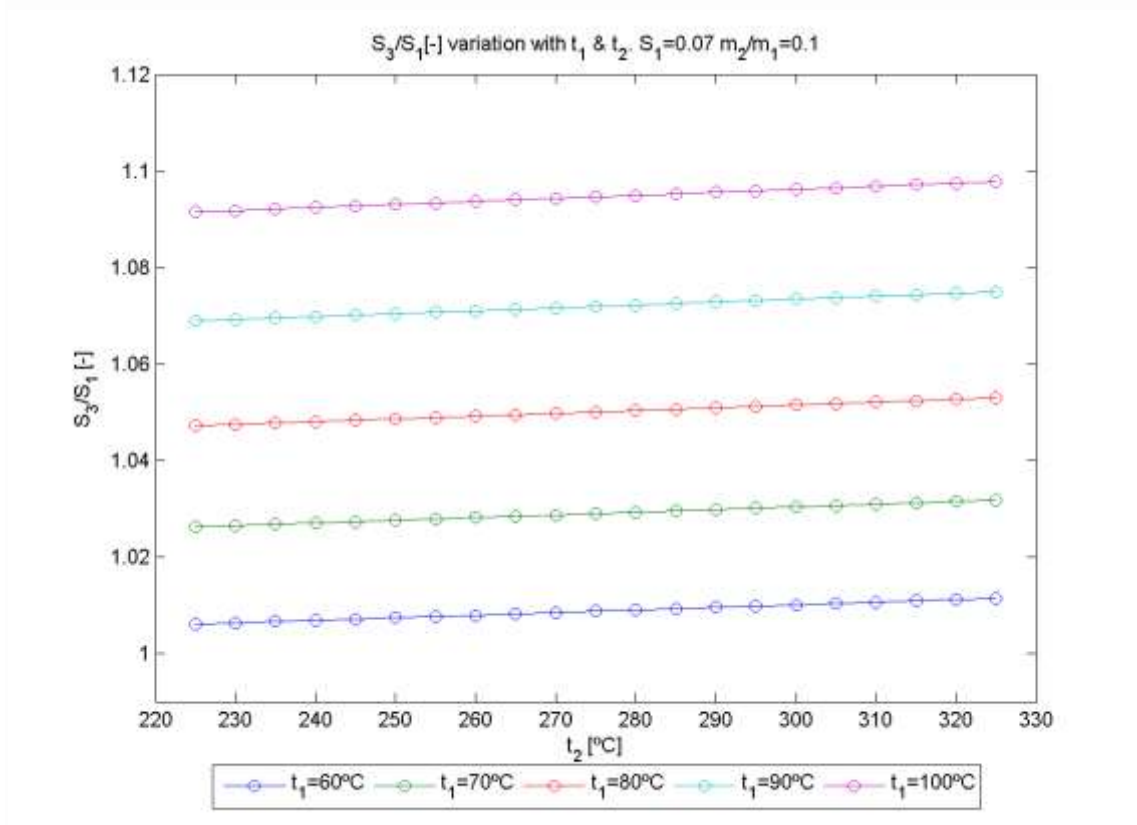


Fig. 8. S_3/S_1 tendency with T_1 , T_2 variations

The salinity of the concentrated brine current (S_3) must be higher than the input (S_1), due to evaporation losses. And therefore, trends in both T_1 and T_2 are similar, is any of them increase them the evaporation does, so therefore increase S_3 . Being therefore the quotient of $S_3/S_1 > 1$ and increasing with the increase of both temperatures.

4.3. Effect of m_2/m_1 ratio in the mass flow m_3

Figure 9 and figure 10 shows the behavior of the oversized flow of the brine current to the output versus the evolution of the temperatures of the combustion gases and brine at the inlet of the control volume for two different values of the ratio m_2/m_1 .

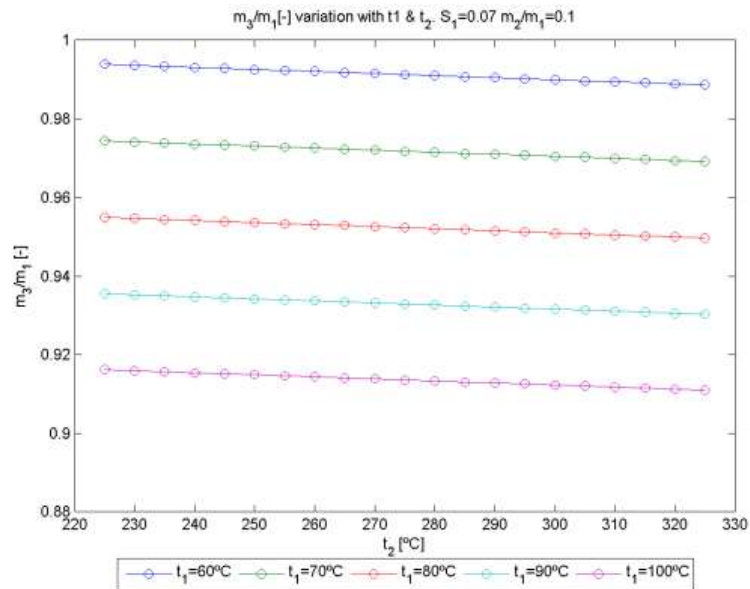


Fig. 9 m_3/m_1 evolution with T_1 , T_2 and $m_2/m_1=0.1$

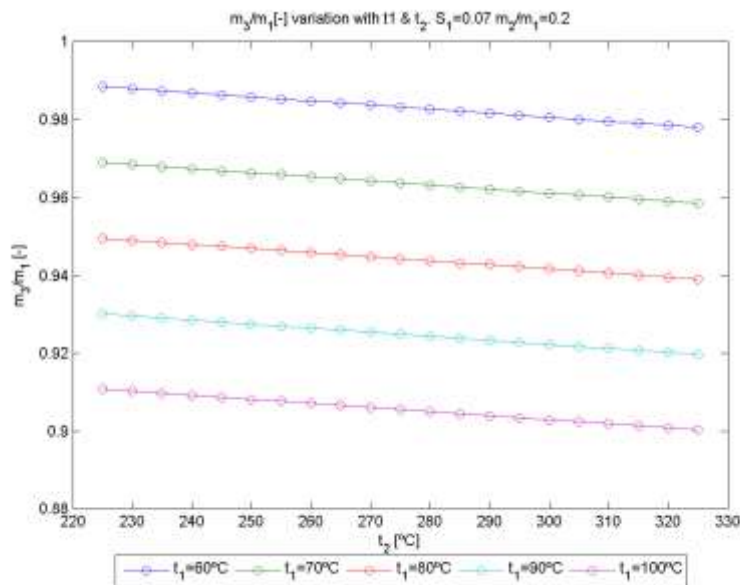


Fig. 10 m_3/m_1 evolution with T_1 , T_2 and $m_2/m_1=0.2$

The effect of increase the ratio m_2/m_1 shows that it is no related to T_1 temperature due to the different between the graph has the same behavior. Nevertheless, as the amount of m_2 increase the heat transferred to the brine increase so the effect of T_2 is more important and increase the amount of water evaporated.

4.4. Effect of m_2/m_1 ratio in the salinity S_3

Figure 11 and figure 12 shows the salinity behavior of the brine current (S_3/S_1), versus the evolution of the temperatures of the combustion gases and brine at the inlet of the control volume for two different values of the ratio m_2/m_1 .

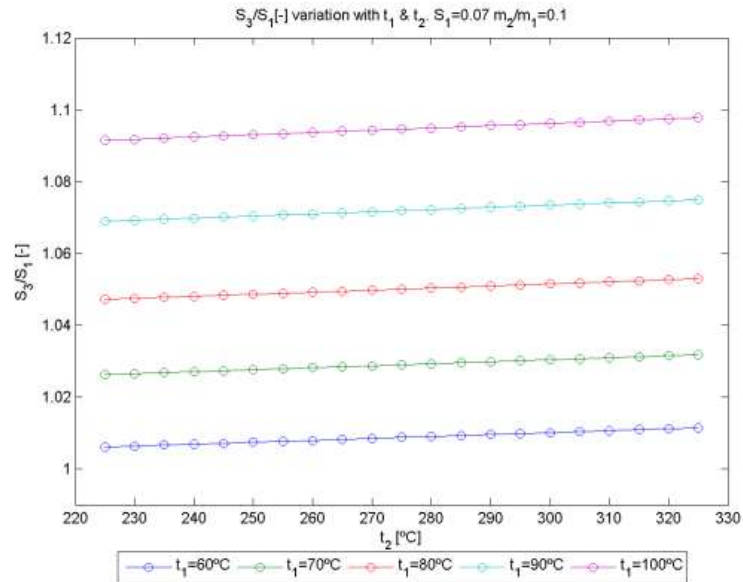


Figura 11 S_3/S_1 evolution with T_1 , T_2 and $m_2/m_1=0.1$

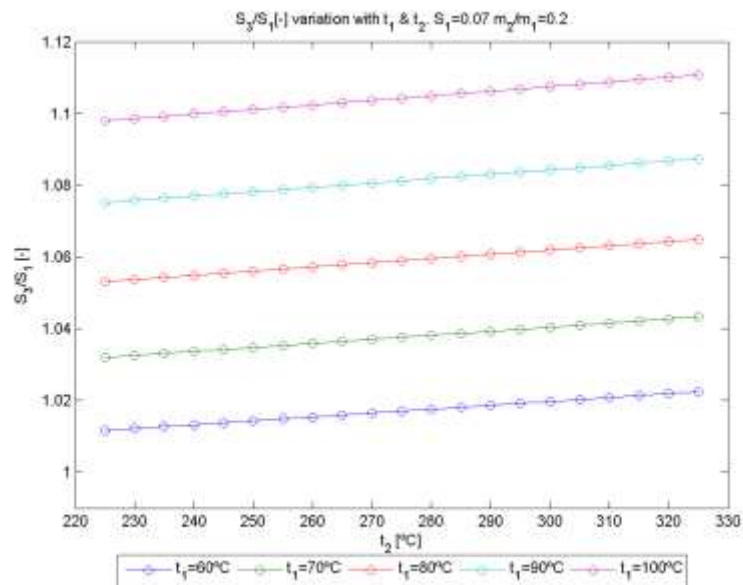


Figura 12 S_3/S_1 evolution with T_1 , T_2 and $m_2/m_1=0.2$

The effect of increase the ratio m_2/m_1 shows that it is no related to T_1 temperature due the different between the graph has the same behavior. Nevertheless, as the amount of m_2 increase the heat transferred to the brine increase so the effect of T_2 is more important and increase the amount of water evaporated so the salinity S_3 increase.

4.5. Effect of S_1 in the salinity S_3

Figure 13 and figure 14 shows the salinity behavior of the brine current (S_3/S_1), versus the evolution of the temperatures of the combustion gases and brine at the inlet of the control volume for two different values of the salinity S_1 .

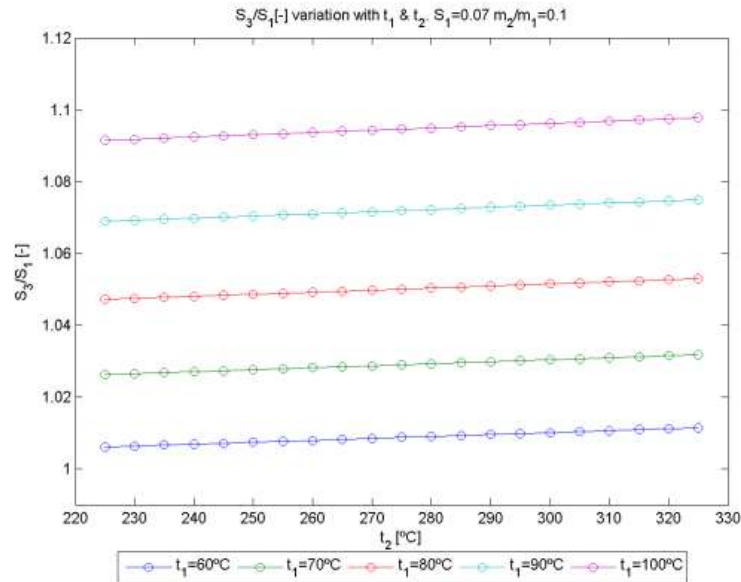


Figura 13 S_3/S_1 evolution with T_1 , T_2 and $S_1=0.07$

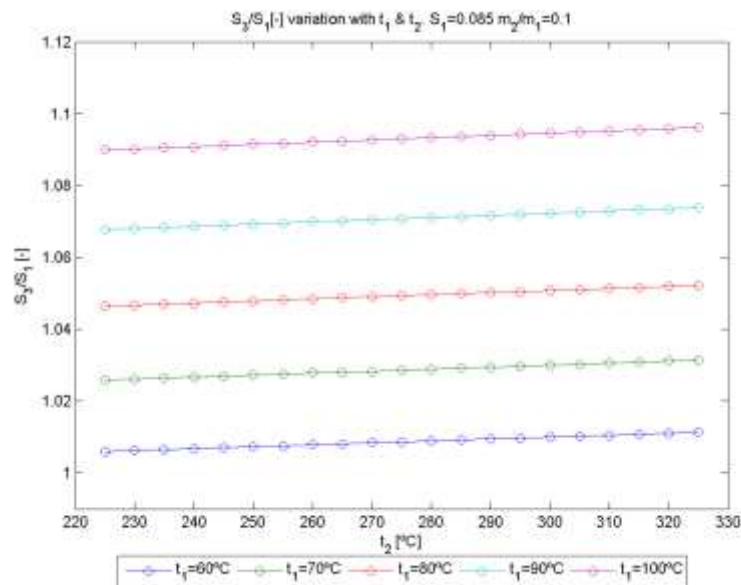


Figura 14 S_3/S_1 evolution with T_1 , T_2 and $S_1=0.085$

The salinity S_1 affect BPE value. For $t=100^\circ\text{C}$ and $S=0.07$ $\text{BPE}=2.16^\circ\text{C}$, if $S=0.085$ then $\text{BPE}=2.94^\circ\text{C}$. This smaller different do not produce any appreciable changes in m_3 , what means that the amount of water evaporated are not modified and therefore neither the salinity S_3 as it is show in the figures 13 and 14. Thus, for the range evaluated there are no effect of S_1 over the parameters m_3 and S_3 .

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