Feasibility study of a Reverse Osmosis Unit at Sines Refinery

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Abstract

This study aims to evaluate the best practices used in the industry for reverse osmosis system, considering its application in brackish water effluent treatment, its advantages and disadvantages. The main goal is to study a reverse osmosis system to treat the blowdowns (currently rejected) from the cooling towers of the Sines refinery, to produce water that can be fed to the boiler. Firstly, it was necessary to calculate the water quality of the cooling towers blowdowns, through a mass balance. Having already known the quality and type of effluent to be treated, the most suitable pre-treatment was chosen and then the reverse osmosis system was designed, using WAVE software, in order to meet the boiler feed water specification. One of the great disadvantages of a reverse osmosis system is the production of a concentrate stream, which will have to be discarded or treated. Thus, a solution was proposed for this concentrate, which was its subsequent concentration in an evaporator and its concentrate to be reused for other industrial purposes, with an associated economic value, assuming a zero liquid discharge vision. Finally, the total fixed investment required for the implementation of the reverse osmosis system of 658k€ and an annual benefit of 322k€ was obtained, concluding that the benefits cover the initial investment in approximately 3 years, with an IRR of 36%, showing the project is economical viable. As for the evaporator, it has a total fixed investment cost of 513.4 k€. However, the global design of reverse osmosis and evaporator proved to be unfeasible, given the IRR value being lower than the actualization rate.

Key-Words: Reverse Osmosis, Water treatment, Membranes, Ion exchange, Zero liquid discharge, Evaporator.

1. Introduction

One of climate change most visible consequences is the increase of the average temperature in the planet, which causes drier winters. This phenomenon entails a reduction in water reserves and leads, in turn, to periods of near-dry in the warmer seasons. Having this in mind, thinking about solutions that minimize the environmental impact is of utmost importance.

Portugal is no exception, spending 4255 million m^3 of water annually, but only 65% of that amount is effectively used. Therefore, there is the need of implementing a strategy for the rational management of the water resources.

Regarding water management in the industrial sector, each company should identify and correct, whenever possible, situations of waste and convert them into situations of reuse/recycling.

In general, in large refineries, water consumption is extremely high. A great contribution to this excessive consumption is the water used in boilers, to produce steam but also the make-up water used in cooling towers. To this equipment converge hot water streams coming from the most diverse operations, carried out in the factory. In this equipment, the water to be cooled meets the air there circulating and the evaporation of part of the water causes its cooling. Associated with this process, however, there is also an undesirable effect which is the increase in the concentration of salts in these waters, due to evaporation.

Periodic blowdowns of these towers are therefore thus essential, requiring, therefore, the introduction of make-up water to lower the solids content and compensate the evaporated flow. These blowdowns can have significant flow rates and are characterized, in general, by a total dissolved solids (TDS) of less than 10000 mg/L, thus making these effluents brackish water blowdowns.

In the case of the Sines refinery, the industrial water used comes from Águas de Santo André and it is subjected to different treatments, depending on the operation for which it is intended. With this work, the main goal is to rethink part of the water cycle in the Sines` refinery, integrating the hot water cooling process with the steam production process. To achieve this objective, the possibility of carrying out the treatment of cooling towers´ blowdowns, using reverse osmosis treatment was studied, as a mean to feed water to the boilers. The study for the sizing of the reverse osmosis system was carried out using the WAVE software.

The use of this tool requires the introduction of data related to each of the streams (tower blowdowns), some of which are provided by the refinery and others are obtained from mass balances.

2. Background

2.1. Blowdowns management Options

Growing urbanization and industrialization has increased pressure on freshwater resources, threatening water quality, safety and ecosystems. Fresh water is used on a large scale, in industry, resulting, in some cases, in the production of large amounts of high salinity wastewater, an example of that is the cooling tower blowdowns [1].

The management options available to dispose cooling tower blowdowns generally depend on water quality, local disposal regulations and the capacity of the treatment processes under consideration. One of the options used in the industry to discard the cooling towers blowdowns is to send it to wastewater treatment processes in treatment plants. This type of treatment is based on phase separation, sedimentation, filtration, chemical/biochemical, oxidation and membrane processes which were applied in order to treat these industrial waters before being discharged as wastewater[2].

Another option found to dispose these streams with high concentrations of salts was to discharge these effluents into evaporation ponds, however, in addition to the need for large areas of land, high environmental regulations prevent salts and other chemical products from being leached into the ground.

Thus, the solution found for the recovery of these wastewaters was the zero liquid discharge (ZLD), which is based on the treatment and reuse of industrial effluents. The ZLD water resources recovery technology has attracted great interest as a promising industrial water management solution, maximizing its recycling. In the ZLD technique, a closed water cycle is created so that no effluent is released from the system, with the possibility of being reused after proper treatment. Many industries admit that the sustainable management of their waters is the only way to fight against the increasingly strict environmental regulation policies and the increasing value of fresh water [3].

In conventional ZLD systems, thermal processes are fundamental, that is, water from industrial blowdowns is fed to a brine concentrator for evaporation and then to a crystallizer. The collected distillate is reused, while the recovered solids are discarded or recovered as by-products. Although these systems have been successfully used they consume, however, a large amount of energy.

Alternatively, the emergence of membrane technology, particularly reverse osmosis (RO) and its combination with thermal ZLD systems has reduced energy requirements.

However, although the incorporation of RO technology can improve energy efficiency, it is only applicable to feed waters up to a certain salinity limit, 70000 mg/L of TDS.

More recently, other ZLD technologies have started to be employed, including membrane distillation (MD), forward osmosis (FO) and electrodialysis (ED).

2.2. Boiler water

The quality of the boiler´s feed water is one of parameters that most affects the safety and efficiency of a boiler, because it can contain different solubilized species, which affect the the adequate operation of the steam generation equipment [4].

Over time, inside the boiler an increase in the solids concentration can occur and the saturation limit for many of these solids can be reached, forcing the occurrence of blowdowns and water makeups more frequently.

Therefore, it is essential to supply the boiler with high quality water so that the equipment does not suffer mechanical problems and that there is no need for high frequency of makeup water. In an efficient boiler system, the recovery of condensed steam and its recycling to the steam generator is extremely important and desirable, given that this water has already been treated and has higher purity than the make-up water, high temperature and low dissolved solids concentration [5]. As not all

steam returns as condensate, the remaining boiler feed must be replaced by properly monitored quality treated water.
The use of high quality feed water is essential, not only to reduce both the use of internal chemicals and the frequency of the occurrence of blowdowns, but also to avoid the occurring of fouling inside the boiler, responsible for corrosion and loss of efficiency.
Water treatment for boilers requires that they have a pH greater than 8.5, and also the removal of corrosive species and low hardness indices as well as alkalinity, carbon dioxide, oxygen and silicon dioxide. The usual specifications for make-up water concentration are present in Table 1.

Table 1- Usual make-up concentration to feed boilers (from[6]).

	Maximum value	Normal value
pH at 20ºC	9,2	8,7
Conductivity (µS/cm)	2	<2
Silicon dioxide (mg/L)	40	20
Iron (mg/L)	10	<3
Oxygen (mg/L)	7	3

2.3. Reverse Osmosis Fundamentals

In the recent decades, processes based on membrane technology have grown rapidly, complementing, or even replacing some of the previous separation processes used in the most diverse industries, namely, chemical, food, pharmaceutical and biotechnology, as well as in environmental and wastewater treatment.
The mechanism of separation used in reverse osmosis is the transfer of mass through a semipermeable physical barrier, the membrane, by the application of a driving force, the pressure. The membrane is placed between two streams, the upstream stream is the feed, and the downstream stream is the permeate. There is also a stream which continues to flow upstream of the membrane after separation that is called the concentrate stream. In water treatment the goal of reverse osmosis separation is to obtain the permeate stream, that is a water with less salts, the undesirable compounds remaining in the concentrate. Equation 1 allows the calculation of the feed (C_f), permeate (C_p), and concentrate (C_c) concentrations and Q represents the flow rate:

$$\begin{cases} Q_f = Q_p + Q_c \\ Q_f . C_f = Q_p . C_p + Q_c . C_c \end{cases} \quad (1)$$

In a RO water treatment process the recovery (R_w) represents the percentage of feed that appears as permeate and the rejection (R_s) refers to the percentage of solute concentration removed from the feed water by the membranes. The most important criteria for determining the performance of the reverse osmosis process are permeate flow and salt rejection, both are influenced by the pressure, temperature, recovery, and feed water composition.

There are some factors that influence the performance of membranes, such as freezing, fouling, scaling and oxidative process by chlorine attack. To minimize these factors in an RO system it is recommended to perform a pre-treatment before the RO unit which allows the increase of efficiency and lifetime of the membranes. The design of this pre-treatment depends on the type of feed water and its composition.

3. Methods and instrumentation

The reverse osmosis system designed to treat the cooling tower blowdowns was modeled by using the WAVE (Water Application Value Engine) software, produced by DuPont in partnership with Dow, which allows modeling three water treatment processes: ultrafiltration, reverse osmosis and ion exchange.
The first input data to the software are the flow rate and the composition of the various ions that constitute the water to be treated. To reduce water hardness the flow rate is fed to an ion exchange column, which was chosen to perform the pre-treatment, before the RO unit. For this purpose, a cationic resin with high affinity for hydrogen was used (AMBERLITE HPR8300 H) as the refinery already uses this type of resin in its demineralization process. Right after, the software requests the duration of each cycle, as well as the desired number of columns in series so 8 hours and 2 columns were chosen, respectively. The regenerating solution was chosen as being HCl and its concentration was 4% (w/w). The HCl quantity added for the regeneration has a safety factor of 10%. The hardness limit was established as 910 ppm CaCO3. Together with the design of the ion exchange column there is also the possibility of adding a deaerator in order to remove the bicarbonate present in the feed water, in this case it was set a concentration of 10 mg/L of bicarbonate in the final effluent (after the deaerator), this result having a safety factor of 30%. Within the software next step is to find possible layouts for the reverse osmosis unit. In this case study, the effluent quality that will result from the reverse osmosis operation is extremely demanding with a recommended

conductivity equal to or less than 2 μS/cm, that is, the "quality" of the permeated water is a crucial factor, as well as its flow rate which should be the higher as possible. Given these requirements, it is easily understandable that, due to the limited separation capabilities and permeation areas of the membrane modules, that are commercially available, it is necessary to manage their number and the configuration of the installation.

In this study, two passages with and two stages each were considered, for the first stage a more permeable membrane was selected, in order to produce the highest possible, permeate flow at expense of a high rejection value.

For the next stages, RO membranes with better performance regarding rejection were chosen. As such, the BW30HRLE-440 module was chosen for the first stage of the first passage, with an area of 40.9 m2/module favoring recovery over rejection. This means that we will have less rejection (99.3%) for the first pass and first stage. For the second stage of the first pass, the BW30XFRLE 400/34 was chosen with an area of 37.2 m2 and a rejection of 99.3%. For the second pass, the modules are the same on both stages, having been chosen the ECO-PRO 440 module with an area of 40.9 m^2 and a rejection of 99.7%. Given that a 75% recovery was assumed, the choice of the number of stages and modules inside each pressure vessel took into account what is recommended in reference [7]:

- For systems with up to 75% recovery, two stages with 6 elements per vessel are common.
- For systems with recoveries between 76 and 87%, two stages with 7 elements per vessel are common.
- For systems with recoveries > 88%, three stages with 6 elements per vessel are the most common.

In separation processes with membranes, an important parameter to consider, is the flow factor. In fact, membranes lose permeation capacity (decrease in flux) as they age. This aging occurs as a result of operating time, pressure, temperature, and reversible or irreversible effects of scale and fouling.

To obtain a constant permeation flux, its decrease must be compensated by a gradual increase in the operating pressure. In the WAVE software, this occurrence is foreseen through the imposition of a flow factor, which can be seen as a safety factor.

The pressure for an ideal system is being calculated when a flow factor of 1 is considered.

In the case of brackish water, the company DOW FILMETEC recommends the use of a flow factor equal to 1 for a new system, an average factor of 0,85 for a 3rd year used system and for an old system (right before changing the membranes) a factor of 0.75 [8]. A flow factor of 0.85 was chosen for all configurations.

4. Results and Discussion

4.1. Feed water to RO

To study an adequate treatment for the blowdowns of cooling towers (AR-X1, AR-X2, AR-X12 and AL-X4) it is essential to have a water report, as complete as possible, of these streams.

In this case study the composition of these streams was obtained through a mass balance.

The mass balance to water in a cooling tower encompasses make-up, evaporation, carryover, and blowdown water streams. Considering the losses that occur through evaporation and the thermal exchanges between water and air, the global mass balance at steady state is given by Equation 2.

$$Q_{make-up\ water} = Q_{evaporation} + Q_{carryover} + Q_{blowdown} \quad (2)$$

This make-up equation can also be described in terms of dissolved salts, as shown in the Equation 3,

$$Q_{água\ make-up} \cdot C_m = Q_{evaporação} \cdot C_e + Q_{arraste} \cdot C_a + Q_{purga} \cdot C_p \quad (3)$$

where the concentration of salts in the make-up water is given by C_m, that the concentration of salts in the evaporation water (C_e) is zero, and that C_p, C_a is the salt concentration in the blowdown and in the carryover, respectively. It is also assumed that the carryover flow is given by Equation 4, [9].

$$Q_{\text{carryover}} = 0{,}001 Q_{recirculação} \quad (4)$$

The average values for the blowdown and make-up flow rates for each tower are indicated in Table 2.

Table 2-Average values of blowdown and make-up flow rates.

Flow rate (m3/h)	AR- X1	AR- X2	AR-X12	AL- X4
Blowdown	19	6,0	6,1	3,7
Make-up	84,7	68,3	35,7	16,2

Using equations 2, 3 and 4 with the values in Table 2, as well as the ionic composition of make-up water, provided by the company, it is possible to calculate the concentration for each ion in the blowdown streams which is shown is Table 3.

Table 3- Composition of cooling towers` blowdowns, obtained by mass balance.

	AR- X1	AR- X2	ARX12	AL- X4
pH	7,9	7,9	7,9	7,8
Hardness (ppm CaCO3)	650,23	1012,15	720,59	606,90
Ca^{2+} (mg/L)	260,10	404,86	288,24	242,76
Mg^{2+} (mg/L)	134,16	208,83	148,67	125,22
Na^{+} (mg/L)	357,68	556,77	396,39	333,85
K^{+} (mg/L)	0,00	0,00	0,00	0,00
SO_4^{2-} (mg/L)	399,90	622,48	443,2	373,2
NO^{3-} (mg/L)	5,60	8,65	6,16	5,20
HCO^{3-} (mg/L)	474,32	738,33	525,65	442,7
SiO_2 (mg/L)	2,78	4,32	3,08	2,60
TOC (mg/L)	8,14	12,67	9,02	7,59
COD (mg/L)	44,43	69,16	49,24	41,47
TSS (mg/L)	6,94	10,81	7,69	6,48
Mn (mg/L)	0,04	0,06	0,05	0,04
Al (mg/L)	0,11	0,17	0,12	0,10
Cu (mg/L)	0,03	0,04	0,03	0,03
PO_4 (mg/L)	0,22	0,00	0,00	0,00
Zn (mg/L)	0,05	0,02	0,02	0,01
Fe (mg/L)	0,06	0,00	0,00	0,00
Cl^{-} (mg/L)	778,16	1211,29	862,37	726,30
Turbidity (NTU)	0,72	1,48	0,76	0,57

Tower blowdowns go to a basin where they mix. This mixture is the stream fed to the reverse osmosis, so the knowledge of its composition is mandatory. The calculation of this composition was carried out using Equation 5, and the data in Tables 2 and 3. The results are given in Table 4, with the respective balance to the ion charges.

$$C_{i,\boldsymbol{basin}} = \frac{\sum_m^K Q_m \times C_{i,m}}{\sum_m^K Q_m} \quad (5)$$

Where $C_{i,\boldsymbol{basin}}$ is the concentration of ion i, in the basin, K represents the total number of blowdowns in the system, Q_m the blowdown flow rate m and $C_{i,m}$ the concentration of ion i in the m blowdown.

Table 4- Quality of the water fed to the pre-treatment (PT).

		Effluent before PT
pH		7,90
Condutivity	µS/cm	4452,00
Phosphate	mg/L	0,12
Chloride	mg/L	863,00
Sulphate	mg/L	443.00
Nitrate	mg/L	6,15
Bicarbonate	mg/L	8,61
Calcium	mg/L	288,14
Magnesium	mg/L	148,62
Sodium	mg/L	396,26
Iron	mg/L	0,03
Zinc	mg/L	0,12
Manganese	mg/L	0,05
Aluminium	mg/L	0,12
Copper	mg/L	0,03
Silicon dioxide	mg/L	3,08
Carbon dioxide	mg/L	28,42
Turbidity	NTU	0,84
TOC	mg/L	9,01
TSS	mg/L	3,08
Hardness	mg/L $CaCO_3$	2194,00

4.2. Pre-treatment

Given the quality of the effluent to be treated, shown in Table 4, a pre-treatment of this water is recommended before entering the reverse osmosis facility. A mainly conventional pre-treatment was chosen, aiming to reduce: total suspended solids, carbonates, free chlorine, metals (Fe, Mn and Cu), organic matter, silicon dioxide and hardness.

The effluent passes through a series of filters to remove total suspended solids to oxidize iron and manganese and form insoluble compounds that can be removed from water (iron filter) and finally, to absorb free chlorine and organic matter (activated carbon filter). As previously seen, next important step is to reduce water hardness. Using the chosen ion exchange resins referred in Section 3, WAVE returns as an output an ion exchange column with a resin volume of 0,93 m3, a capacity of 2353 equivalents and a specific velocity of 38 BV/h. The stream from the ion exchange column is fed to a deaerator where the concentration of carbonates is reduced to 12,59 mg/L. Table 5 shows the final quality of water before entering in RO.

Table 5- Quality of the water fed to RO system.

		Treated effluent
pH		8,8
Conductivity	μS/cm	3868
phosphate	mg/L	0,12
Chloride	mg/L	916,6
Sulphate	mg/L	443
Nitrate	mg/L	6,15
Bicarbonate	mg/L	12,59
Carbon dioxide	mg/L	0,02
Calcium	mg/L	197,12
Magnesium	mg/L	101,67
Sodium	mg/L	396,26
Zinc	mg/L	0,84
Aluminium	mg/L	0,17
Copper	mg/L	0,00
Free chlorine	mg/L	0,00
Silicon dioxide	mg/L	3,08
Turbidity	NTU	0,00
TOC	mg/L	2,00
Q	m^3/h	33,0
Hardness	mg/L CaCO3	910,96
TDS	mg/L	2078
LSI	mg/L	0,50
SDI	mg/L	0,55

To adjust the pH of the effluent from Table 5 and minimize calcium carbonate scaling 6,30 mg/L of hydrochloric acid 32 %, is added. It`s recommended the use as well of an antiscaling agent to minimize possible scaling of calcium compounds. Before the effluent be fed to the RO installation it is also common to pass it through a microfiltration filter, in this case the model PD-1-40 was chosen.

4.3. RO system

After some preliminary simulations, the best results were obtained for a configuration with two passages and two stages in each passage and recirculating the concentrate from the second pass to the first. This recirculation will change both the flow rates and the total dissolved solids concentration in the feed water to be fed to the RO installation in each simulation.
This improvement obtained with the recirculation is explained by the fact that in small reverse osmosis systems, as is the case, the flux is not high enough to make a good sweep of the membrane surface. When part of the concentrate is added to the feed, the flow increases and so the recovery of each individual module decreases which reduce the fouling potential. In the design of the system, an interstage pump was also considered in the first pass to control the flow in the second stage and reduce the potential of scaling.
Once this final configuration was chosen three recovery values 65%, 75% and 85% were simulated.

4.3.1. Recovery of 65%

For a 65% recovery, the system configuration, optimized by WAVE is composed of two passages, each with two stages. The first stage of the first passage has four pressure vessels and the second only two. The second passage has two pressure vessels on the first stage and only one on the second stage. All pressure vessels are composed of six elements. This system has a feed flow rate of 36.3 m^3/h with an initial quality in TDS of 1918 mg/L. It has a recycling of the concentrate from the second pass to the first pass of 3.32 m^3/h and produces a permeate flow rate of 21,4 m3/h with a quality of 1.0 mg/L.
The fouling rate within a membrane system depends on the permeate flux in each membrane element. The first elements within a pressure vessel generally produce the highest permeate fluxes, this is due the fact that these membrane elements are exposed to the lowest total dissolved solids feed water and to the highest membrane feed pressure. The effect of pressure drops and the increase in the feedwater TDS can significantly affect the productivity of membranes located on the second stage, leading to flux imbalance. To reduce this effect a booster pump was added to increase the feed pressure to the second stage of the first pass and then balance the flux. To feed the first stage of the first pass, it is necessary to supply a pressure of 6.6 bar. The average flux for this passage is 17L/m^2h. The average total dissolved solids in the permeate from the first pass is 46.2 mg/L showing that two stages per pass would not be sufficient to treat the feed to the desired specification. Thus, the permeate of the first passage goes to a second passage, also consisting of two stages, being fed to the first stage of the second passage with a pressure of 8.5 bar. The final permeate flux (output of the second pass) is 21.5 L/m^2h. It presents a total dissolved solids of 1.0 mg/L and a conductivity of 1,4 μS/cm at 25°C.

4.3.2. Recovery of 75%

To increase the final, permeate flow rate, the RO operation was simulated for a recovery factor of 75%, keeping the previous configuration, that is, two passages, with two stages each, but changing the number of pressure vessels (PV). Thus, the first stage of the first passage is composed of five pressure vessels and the second of only three. The second passage consists of two PV on the first stage and only one on the second stage. All pressure vessels are composed of six elements. In addition, an interstage pump continues to be used in the first pass, which increases the pressure of the concentrate in the first stage by 2 bar.

To supply the first stage of this RO system configuration, it is necessary to supply a pressure of 7 bar. The average flux for this passage is 15 L/m2h. The average total dissolved solids in the permeate from the first pass is 84.2 mg/L.The permeate of the first passage follows to a second passage, also consisting of two stages, being fed to the first stage of the second passage with a pressure of 9 bar and the average flux in this passage is 32 L/m2h. The total permeate for this system, presents a total dissolved solids of 1.01 mg/L and a conductivity of 1.5 μS/cm at 25°C.

4.3.3. Recovery of 85%

A 85% recovery was also, simulated again for two passages, with two stages each. In this case, a pump power of 3 bar was used between the stages of the first pass, to compensate for the pressure drop that occurs in the first stage. The first stage of the first passage is composed of five pressure vessels and the second only three. The second passage consists of two pressure vessels on the first stage and only one on the second.

This system has a feed of 46.9 m3/h and a total dissolved solids of 4308 mg/L. In addition to recirculating the concentrate from the second pass to the first pass, 11.5 m3/h of the concentrate from the first pass was also recycled. Therefore, a permeate flow rate of 28.3 m3/h with a quality of 1.11 mg/L was obtained using 7 elements per pressure vessel. It was obtained a concentrate flow rate of 5 m3/h with a total of dissolved solids of 13824 mg/L.

The average flow for the first passage is 15 L/m2h and the average total dissolved solids in the permeate from the first pass is 147.3 mg/L. Thus, the permeate of the first passage goes to a second passage, also consisting of two stages, the first stage of the second passage fed with a pressure of 11 bar, as shown in Table 29. The average flow in this passage is 31 L/m2h. The permeate flow rate has a total dissolved solids of 1.11 mg/L and a conductivity of 1.6 μS/cm at 25ºC were obtained.

From the study carried out with the three recovery rates it can be concluded that to a higher recovery rate corresponds a higher permeate flow rate of treated water to be fed to the boiler. However, a higher recovery rate leads to a greater number of modules and membranes (higher equipment cost), higher energy consumption and lower permeate quality. The quality of water to feed boilers is the most important requirement, in parallel with the permeate flow, so the recovery rate that best meets these two requirements is 75%. To confirm this conclusion sensitivity analysis encompassing the three recovery values was made.

4.4. RO System Sensitivity Analysis

The final values obtained for this work, are function of the parameters of the feed water that enters in the installation and the quality required for the final product. Throughout the process, decisions must be made regarding the configuration of the plant, but some of these decisions are made based on values advised by the software. In this context, the final values could be different if different input values were given and different decisions were made, so a sensitivity analysis was performed to assess the response of the system to the variation of some parameters which are considered very important for the performance of the operation. Among the most important parameters are the flow factor, the concentration of silica, calcium, total dissolved solids, and the feed flow rate. Within this context there are two classes of parameters, namely those that influence the correct operation of the RO installation and those that influence the final quality of the permeate (TDS analysis). Although this sensitivity analysis was made for all three values of recovery, only the results for 75% will be presented.

4.4.1. Flow factor

Flow factor is related to flow which, in turn, depends on temperature. This why both parameters have to be analyzed together with results shown in Figure 1. Two situations were analyzed i) most favorable (FF = 1 and 25°C) and ii) most unfavorable (FF = 0.75 and 20 ºC)

As expected, an increase in temperature decreases the power required for both the first pass (pump 1) and the second pass (pump 2) feeds. As is very well known permeate flow is directly proportional to temperature with a 3% change for each 1ºC change in temperature[8]. This can be explained because the viscosity of water decreases with temperature, making it easier to pass through the membrane.

The pump chosen for the first pass must have powers of 12,5 kW and 10,5 kW to adjust situation ii) and i) respectively. For the second pass, the pump should have a power of 11,5 Kw and 8 kW to adjust to ii) and i) situations, respectively.

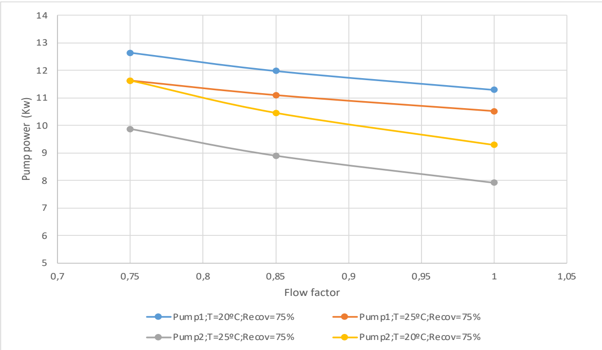

Figure 1- Variation of power pump with flow factor for a 75% recovery.

4.4.2. Silica

It is very important to control the silica content in the RO feed, given its high tendency to scaling. This tendency, which is directly related to the operating temperature is evaluated through

the % saturation obtained in the concentrate, as result of four hypothetical concentrations of silica in the feed stream. The results can be seen in Figure 2 for a range of temperatures from 15 to 25 ºC and for a 75 % recovery.

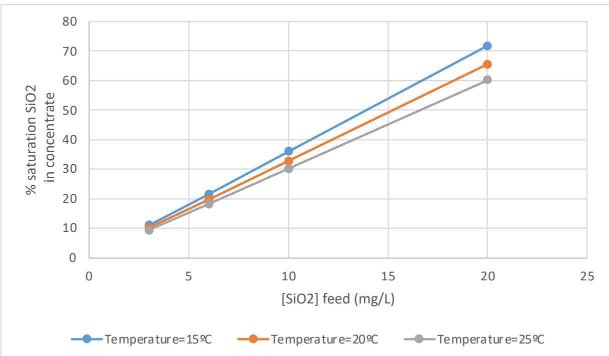

Figure 2- Influence of silica feed concentration in the % of silica saturation in the concentrate for 75% recovery.

As can be observed, for the higher feed concentrations a 10ºC difference makes the % silica saturation vary by 11%. It is also possible to see that a variation in silica content from 2.5 mg/L to 20 mg/L in the RO feed makes the degree of saturation increase from 10% to approximately 65%.

4.4.2. Calcium

Calcium is another component of RO feed that must be permanently controlled as it promotes scaling as well.

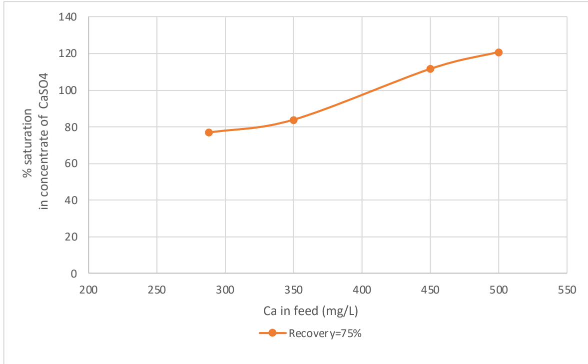

Figure 3- Influence of calcium feed concentration in the % of calcium sulphate saturation in the concentrate for 75% recovery.

The influence of temperature on the calcium saturation percentage was also studied and was shown (results not presented) to be null, that is, the calcium sulfate saturation rate is independent of temperature. It depends only on the initial feed calcium concentration. For feed concentrations in the range of 270 to 500 mg/L, the results in Figure 3 allows to conclude that a significant variation from 60% to 20% in the percentage of calcium saturation is obtained. A significant increase from 350 mg/L can be observed meaning a higher potential risk of scaling.

4.4.3. Total dissolved solids

During the RO operation, total dissolved solids concentration (TDS) increases at the membrane surface thus resulting in an osmotic pressure increase, as well. As a consequence, driving force for permeation decreases as well as permeation flux. So, less water passes through the membrane resulting in a higher concentration of TDS in the permeate. TDS can be estimated by the electrical conductivity of the solution, in μS/cm, when the pH is between 6.5 and 8.5 according to Equation 6.

$$\mathrm{TDS} = 0{,}68 \text{ x Condutividade} \quad (6)$$

To be adequate for boiler feeding, water has a tight specification, that is, a conductivity of 2 μS/cm (approximately a TDS of 1.4 mg /L).

So, this analysis is focused on how much TDS can be tolerated, in the concentrate side of the OI membrane, as to provide a permeate with enough quality to feed a boiler.

The results of the simulation, always considering a 75% recovery, are shown in Figure 4 where it can be observed that a TDS content of up to 3232 mg/L on the concentrate side of the membrane can be tolerated.

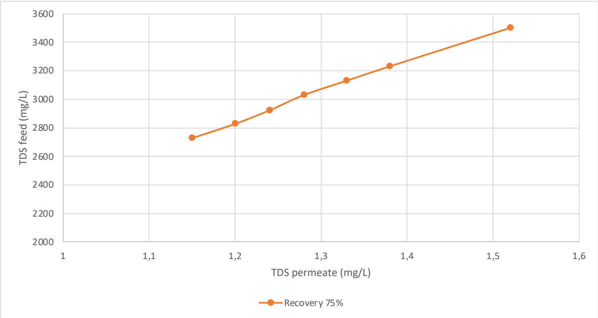

Figure 4- Influence of TDS feed concentration in the TDS permeate flow rate for 75% recovery.

4.4.4. Flow rate

Anticipating possible changes in flow rates to be treated, a very simplified sensitivity analysis was carried out for this parameter. An increase in the flow rate is expected to have an impact on the number of elements that make up the installation and in their arrangement. The results of the simulation showed that there is a direct proportionality between the number of elements and the capacity (flow rate) with a proportionality constant of about two.

This increase in the number of elements needed has an impact both on equipment costs, and on energy consumption, related to pumping.

In figure 5, it is possible to observe energy consumptions for plants with capacities above 500 m/day. A significant dispersion the results obtained with the simulations, exists but a pattern can, nevertheless, be observed. From this pattern, it can be concluded that the consumption (relative to a cubic meter of treated water) of the largest plants is mostly between 0.95 and 1.05 kWh/m^3. This consumption can, however, be reduced by recovering part of the energy, transported by the concentrate due to its high pressure. Passing this stream through a Pelton turbine, for example, around 90% of the energy can be recovered and reused, assuming pump and turbine efficiencies of 75% and 90%, respectively.

All simulations which were performed showed that energy consumption is independent of capacity, and much lower when using an energy recovery device. On average, for a recovery of 75% the consumption required decreases to 0.5 kWh/m^3.

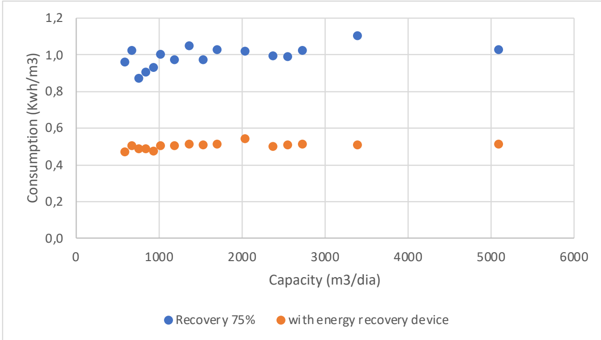

Figure 5- Energy consumption for a 75% recovery with and without energy recovery device.

4.5. Concentrate treatment

A reverse osmosis operation always leaves behind a concentrate with a high salt content for which, a treatment solution must be found.

One possibility, here proposed, to reduce the flow rate of saline water discharged, is the use of an evaporator with vapor recompression. Evaporation is an energy intensive operation but if the steam produced within the evaporator is captured and compressed, it can be recirculated and used as heating steam. In this process, it was decided to add part of the condensate to the superheated steam from the compressor, so that it could join the saturated steam from the network. For the design of this equipment, steady state conditions were considered, and the dilution enthalpy and energy losses were disregarded, as well as the presence of salts in the evaporated. A value of 15ºC was considered for ebullioscopic elevation, slightly lower than that of sea water. The evaporator could treat, as well, the 48 m3/h of saline water that are produced daily from the regeneration of the ion exchange columns (with a TDS=10642 mg/L). This regeneration is a discontinuous operation, so a buffer tank is needed to feed the saline water continuously to the evaporator. These blowdowns which will be fed, to the evaporator, together with the flow of concentrate from the reverse osmosis system.

Table 6 shows the condensate flow rate used to cool the supersaturated steam, and the flow rate of make-up as well as the condensate flow rate to be reused as boilers feed together with the RO permeate. For the calculation of compressor power an efficiency of 75% was assumed.

Table 6- Results of evaporator project.

Q condensate (Kg/h)	2190
Q make-up from the net (Kg/h)	2,90
Q pure water (Kg/h)	7145
Power of compressor (kW)	531

Despite the intensive energy consumption, this evaporation process reduces the flow rate of concentrate produced, in 70%. In addition to the significant reduction in heating steam consumption, a flow rate of 7.1 m^3/h of pure water is produced which can be fed directly to the boilers. Efforts have recently been made to reduce the costs of demineralization processes such as the recovery of materials remaining in the concentrate from the evaporator, which is rich in products with calcium, magnesium, silica and sulfates and to explore a commercial application such as its use in cement industry [10].

5. Economic analysis

The economic analysis included the calculation of the required total fixed investment and economic benefits from the implementation of the reverse osmosis system, considering that the unit will be subject to a total shutdown of 30 days per year. The total fixed investment required, including direct and indirect costs, is 657 k€. Direct costs include base equipment, piping, control equipment, electrical installations, buildings and assemblies. Provision for contingencies was the only indirect cost considered. The specific cost (cost per m^3 of water produced) is 0.84€, with a total annual operating cost of 322 k€ for the RO system. The total benefit from the reverse osmosis system is 322 k€/year and includes the benefit of reducing regenerant consumption and the decrease of the water consumption of the current demineralization system of the refinery. The payback calculated for the RO project was 3 years and the IRR was 36%. It was also calculated that the total fixed investment required, in case an evaporator was chosen, to reduce the concentrate flow rate discarded, reaching a value of 513 k€ for this equipment and 363 k€ for annual operating cost. However, the incorporation of an evaporator revealed to be economical unfeasible.

6. Conclusion

The study concluded that the system recommended to implement at the Sines refinery to treat blowdowns from the cooling towers will be a reverse osmosis system with two stages and two passages with a recovery rate of 75% and a permeate flow rate of 25 m3/h. To increase the efficiency of this system and to reduce fouling and membrane degradation it is necessary to use a pre-treatment that includes a multimedia filter, an iron filter, an activated carbon filter, a microfilter and a system of ion exchange to reduce the hardness of brackish water fed to reverse osmosis. The water leaving the reverse osmosis meets the quality requirements to be fed to the boilers. For the incorporation of this reverse osmosis system in the refinery, a total fixed investment of 657 k€ will be necessary with a total benefit of 322 k€/year, with the investment being recovered in 3 years.
To treat the saline blowdowns, it was proposed to send them to an evaporator with vapor recompression.

6. References

[1] "Zero Liquid Discharge - ZLD." https://www.lenntech.com.pt/processes/Brine-Treatment/zero-liquid-discharge-zld.htm (accessed Aug. 20, 2021).

[2] Muhammad Yaqub and W. Lee, "Zero-liquid discharge (ZLD) technology for resource recovery from wastewater: A review," *Sci. Total Environ.*, vol. 681, pp. 551–563, 2019, doi: 10.1016/j.scitotenv.2019.05.062.

[3] C. Charisiadis, "Brine Zero Liquid Discharge (ZLD) Fundamentals and Design," *Lenntech*, pp. 1–76, 2018.

[4] Realpars, "WHAT IS A BOILER AND HOW DOES IT WORK?" https://realpars.com/boiler/ (accessed Jul. 10, 2021).

[5] Spirax Sarco, "THE BOILER HOUSE." https://www.spiraxsarco.com/learn-about-steam/the-boiler-house (accessed Jul. 10, 2021).

[6] Lenntech, "Characteristics of boiler feed water." https://www.lenntech.com/applications/process/boiler/boiler-feedwater-characteristics.htm (accessed Oct. 23, 2021).

[7] DeMichele Don; F. Seacord Thomas, "Manual of Practice.pdf," Texas. [Online]. Available: https://www.twdb.texas.gov/publications/reports/contracted_reports/doc/1148321310_Manual of Practice.pdf (consultado: 20-03-2021).

[8] J. Kucera, *Reverse Osmosis Industrial applications and processes*. Co-published by John Wiley & Sons, Inc. Hoboken, New Jersey, and Scrivener Publishing LLC, Salem, Massachusetts, 2010.

[9] R. . Perry, *Perry's Chemical Engineers' Handbook*, 7th ed. 1997.

[10] H. Lee *et al.*, "Recycling of reverse osmosis (ro) reject water as a mixing water of calcium sulfoaluminate (csa) cement for brick production," *Appl. Sci.*, vol. 9, no. 23, 2019, doi: 10.3390/app9235044.