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MEMBRANE SELECTION CRITERIA FOR SEAWATER DESALINATION BY REVERSE OSMOSIS

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ABSTRACT

Seawater desalination is a technology with a high-speed evolution for obtaining drinking water from seawater, especially in vulnerable areas of the globe. Reverse osmosis is the most used technology and is supported by the commercial development of many types of membranes widely used in desalination. However, there are no general rules for membrane selection. A single criterion is generally accepted: the membrane's permeability to the salts in the feed (generally to sodium chloride). This article has three specific aims: 1) experimental determination of the salt content of the water of four selected seas (i.e., Paralia Katerini – Greece, Civitavecchia – Italy, Tunis – Tunisia, and Manifah – Saudi Arabia). 2) from an extensive range of commercially available membranes, after consulting several "technical data sheets", four types of membranes were selected for this study: Hydranautics SWC6 - LD, Koch TFC - HF - 8", Toray TM820V - 400. Our calculation regarding their permeabilities led to values in the range of 0.61 liter/m^2·h·bar to 1.87 liter/m^2·h·bar. 3) for each selected membrane, the total area required in a RO plant to obtain a permeate flow of 1 000 m^3/day and a salt concentration in the permeate of 225 ppm was calculated for an operating pressure in the range of 35 bar to 65 bar, for operating temperature in the range of 20°C to 50°C and for seawater salinity in RO feed in the range of 30 000 ppm to 50 000 ppm. The concentration of salts in the feed and the operating pressure have the most significant influence on the increase in the total area of the membranes in the reverse osmosis plant.

Keywords: seawater, membrane, reverse osmosis

INTRODUCTION

Currently, access to water resources is a severe problem for many of the world's states, due to its unequal distribution and how governments and the local population manage it. The impact of this unequal water distribution on the globe is felt in several areas of human activity, from agriculture and industry to health and quality of life [1]. Thus, if an American consumes, on average, 600 liters of water per day, an African consumes only 10 liters. Specialists claim that a population that benefits from drinking water sources below the value of 1700 m^3/year/inhabitant is under water stress [2]. Unfortunately, a large part of the world's population finds itself in this situation. In some countries, the water shortage crisis already has catastrophic proportions.

The crisis of drinking water resources is more than evident if we also consider that although 72% of the Earth's surface is covered by water, more than 97% is salt water. The estimates of specialists from the Woods Hole Oceanographic Institution - WHOI, Massachusetts, USA, show that there are now approximately 1.332 billion cubic kilometers of water on Earth. Fresh water trapped in glaciers represents 70% of this estimate, and less than 1% of the fresh water on the planet is accessible [1].

The evolution of fresh water consumption confirms human evolution, so if at the beginning of the last century, the average consumption was only 240 cubic meters over the entire period of an individual's life, in recent years, the consumption has almost tripled, according to modern living standards. The crisis of water resources is determined by certain factors, among which we can mention the demographic explosion. This fast urbanization process led to significant population agglomerations, especially to the increased need for fresh water in industry and agriculture.

In the context of the current economic development and the higher and higher targets that economic agents set year after year, it is estimated that the need for (fresh) water will be higher, and the reserves will be lower.

With certainty, the leading cause which determined the upward curve of current water needs and consumption, is technical progress, so that industry and agriculture swallow most of the world's water consumption. It is estimated that the shortage of water and its distribution will affect at least half of the world's population starting from the year 2030. Thus, the water crisis can cause major conflicts among the affected populations [2, 3].

Desalination is a generally accepted process for obtaining potable water from seawater, which justifies the fact that its application is growing rapidly. Following this process, the salt content of the sea water is significantly reduced. However, in order to obtain potable water that can be distributed through pipelines for population consumption, the desalination product must be partially reconstituted from the point of view of some vital salts for human consumption [3]. Therefore, unlike natural waters that have variable, harmful compositions, desalinated water has a controllable composition.

The race to build seawater desalination plants started as early as 1975 when there were already around 1036 such plants worldwide, with a production of 2.1 million m^3/day. In 1991, their number reached 2154 units, with a daily capacity of 6.8 million m^3/day [2]. Today, 19 000 units in operation generate over 100 million cubic meters of freshwater per day worldwide. The countries in the Gulf area have the most treatment plants. For example, Saudi Arabia (the Jubail Plant) generates 1.4 million m^3 of freshwater per day, in the United Arab Emirates 800 000 m^3/day, Kuwait produces 600 000 m^3/day while Iran produces100 000 m^3/day [3, 4]. In Europe, desalination technology works in countries such as Italy, Greece, Belgium, Holland and Spain [5].

Many effective desalination technologies are known today. All of these aim to produce a stream of water with a low concentration of salt (called the product stream) and another with a high concentration of salts (called the concentrate or brine stream).

Today, industrial technologies for salt separation based on distillation or membrane separation are successfully applied [4, 5, 6].

This work aims to demonstrate and discuss several critical criteria for membrane selection in seawater desalination through reverse osmosis (RO). The most important property of a membrane is its permeability toward the majority component in seawater, sodium chloride. First, the salt content of the water from four seas is experimentally determined. Then, four types of commercial membrane modules are selected for which the permeability is calculated.

Finally, in this work, the variation of the membrane's area in the RO process was also studied according to the influence of pressure, salt's feed concentration, and working temperature. If the feed pressure is an operating parameter related to the economy of the process, then, the other two factors are associated with the geographical location of a desalination plant based on membrane technology.

MATERIALS AND METHODS

Composition of sea and ocean water

It is well known that seawater is salty. In fact, it constitutes a complex solution where a very large number of ions are mixed. As a rule, its composition remains the same in all oceans; high-resolution analyses demonstrate a small local variation of it [5].

The total amount of salts that seawater contains is called salinity; it is expressed in % or parts per million (ppm). On average, seawater has a content of 3.5% salts (3.5g of salts per 1 liter of water). Specialists prefer to express salinity in ppm, hence the average of 35 000 ppm (35 mg of salts per 1 000 ml of water) [5]. Any chemical element can be found in sea water. It should be noted that the salinity of sea water is always given by the same types of ions. Therefore, even if the salinity is different from the average, the ions are always in the same proportion (Figure 1).

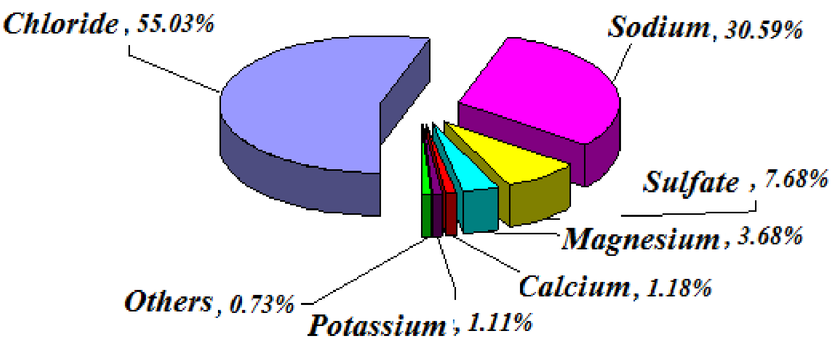

Figure 1. *The proportion of ions (in weight %) in seawater* [7].

The predominant salt in seawater is sodium chloride, but there are other salts as well (see Figure 2).

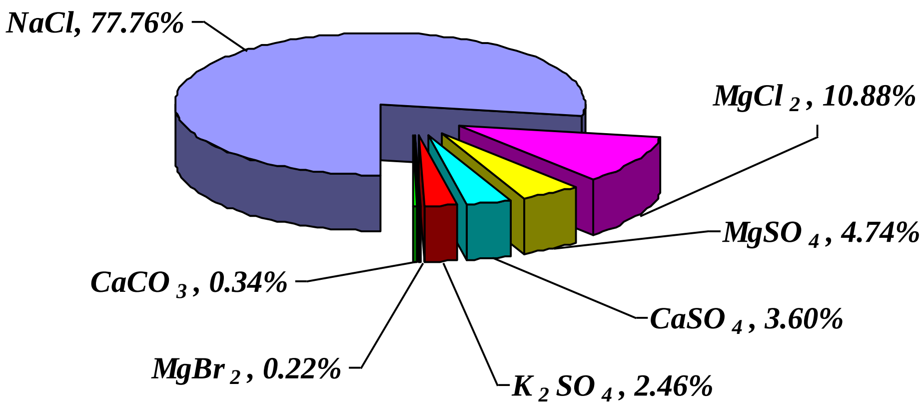

Figure 2. *The proportion of salts (in weight %) in seawater* [1].

Not all seas and oceans are the same (Table 1). There are variations in time and space of the salinity of sea waters.

Table 1. *Salinity in different areas of Earth's seawaters and Oceans* [2].

Baltic Sea	6 - 18 g / l
North Sea	32 g / l
Oceans	33 - 37 g / l
Mediterranean Sea	36 – 49.5 g / l
Red Sea / Persian Gulf	39 - 52 g / l
Dead Sea	230 g / l

The variations in the salinity values of the oceans are due to several factors. Water evaporation or the amount of precipitation in the ocean area are the most important factors. Since salt does not evaporate in the atmosphere, in the case of conditions that favor increased evaporation, the consequence is that salinity increases. If there is more precipitation, then the salinity decreases. Another factor that can change salinity is the discharge of freshwater into seas and oceans. If freshwater tributaries have lower flows, sea currents will quickly mix them with ocean water and have little effect on ocean salinity. However, large freshwater rivers such as the Amazon can cause a low salt content when discharged into the ocean. Melting of large glaciers (consisting of freshwater and devoid of any salt) will also reduce salinity while freezing of seawater will temporarily increase salinity.

The seawater temperature knows major variations, also. The northern basin of the Indian Ocean has the warmest water on Earth's vast seas and oceans, while near the poles the sea water reaches freezing temperatures. In the warm half of the year, near the southern shores of Asia, the ocean water reaches thermal values of over 30°C on the surface. By the way, in the area of the Persian Gulf, the highest average temperature of the waters of the Planetary Ocean was recorded, 35.6°C in August [1].

Experimental determinations of seawater salinity in critical geographic areas

In order to determine the salinity, surface water samples were collected from three points located in the Mediterranean Sea basin (i.e. Paralia Katerini - Greece, Civitavecchia - Italy and Tunis - Tunisia) and one point located on the coast of the Persian Gulf (i.e. Manifah - Saudi Arabia).

The experimental determination was made based on the reaction between chloride ion and silver nitrate in the presence of potassium chromate.

The reactions that take place are the following:

$$Cl^- + AgNO_3 \rightarrow AgCl + NO_3^-$$

$$CrO_4K_2 + 2AgNO_3 \rightarrow CrO_4Ag_2 + 2KNO_3$$

The reagents used were:

- silver nitrate, 0.1 N solution;
- potassium chromate, 10% solution.

The procedure was as follows: 25 ml of water were taken from each sample and placed in an Erlenmayer beaker. Next, 1 ml of potassium chromate solution was added to the water sample. This was followed by treatment with 0.1 N silver nitrate solution until the color turned from yellow-green to brick. The following equation was used to calculate the chloride ion content:

$$\text{mg } Cl^- / l = (V \cdot f \cdot 3.55 / 25) \cdot 1000 \tag{1}$$

where:

V- volume of the silver nitrate solution introduced into the titration sample;

f - correction factor of silver nitrate solution, *f* = 1;

3.55 - the equivalent in mg Cl^- of 1 ml of silver nitrate solution, 0.1 N.

After the analyses, the following volumes of $AgNO_3$ 0.1 N solution were consumed and the following values were obtained for the analyzed ion (with equation 1):

- Paralia Katerini – V = 149 ml => 21.2 g / l Cl^- ;
- Civitavecchia – V = 153 ml => 21.7 g / l Cl^-;
- Tunis – V = 148,5 ml => 21.1 g / l Cl^-;
- Manifah – V = 196 ml => 27.8 g / l Cl^-.

Considering the value of the Cl^- ion as 55.03 weight% of the total dissolved ions and considering the data from Fig. 2, the salinity values, and the proportion of salts in the analyzed waters were calculated (Table 2).

Table 2. *Calculated values and salinity composition of the analyzed waters.*

		Paralia Katerini	Civitavecchia	Tunis	Manifah
Components	weight%	ppm	ppm	ppm	ppm
Cl-	55.03	21.2	21.7	21.1	27.8
Total dissolved ions	100	38524	39433	38343	50518
Na Cl	77.76	29957	30663	29815	39283
$MgCl_2$	10.88	4191	4290	4172	5496
Mg SO_4	4.74	1826	1869	1817	2395
$CaSO_4$	3.60	1387	1420	1380	1819
K_2SO_4	2.46	948	970	943	1243
$MgBr_2$	0.22	85	87	84	111
$CaCO_3$	0.34	131	134	130	172

The seawater salinity values for the geographical points studied can also be found in Figure 3.

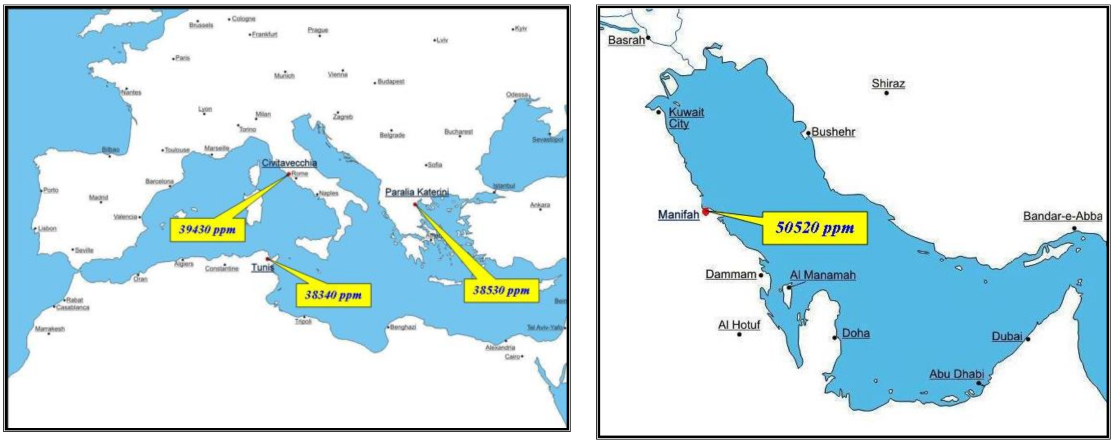

Figure 3. *Experimentally obtained values of the salinity of waters from the Mediterranean basin and the Persian Gulf.*

RESULTS AND DISCUSSIONS

Membrane selection according to the physico-chemical characteristics of seawater

For the design of a reverse osmosis system, in addition to optimizing flows and configuring a system of membrane modules, membranes must be selected that ensure the process's efficiency according to the desalination plant's working conditions.

A successful desalination system requires a correct understanding of the RO process parameters, and the RO design must be adapted to the concentration of salt in the seawater and its temperature at the working point of the desalination plant but with as little energy consumption as possible [5].

Among the characteristics of the membrane modules, the most important, are as follow [8]:

- membrane surface (determines the number of modules for a particular required membrane area);
- membrane permeability (determines the membrane area required for a specific permeate flow rate);
- salt retention (determines the concentration of salt in the permeate);
- recovery rate (determines the efficiency of the installation, which can be improved by choosing an optimal configuration of the module system;
- maximum working temperature;
- maximum working pressure.

This work aims to analyze the influences of the following parameters over the membrane area:

- the concentration of salt in the feed of the reverse osmosis plant (which is related to the geographical location of the RO plant);
- the working temperature of the plant (also related to the geographical location of the RO plant);
- operating pressure (with direct impact on the energy consumption of the RO plant).

First of all, from a large range of commercial available membranes, were consulted many „technical data sheets" and, finally, for this study was selected four types of membranes: two with general recommended as medium permeability and other two recommended as high permeability, all with the same geometric dimensions (length 40" and diameter 8") and the same useful surface/per RO element = 37 m^2 [9, 10, 11]. The commercial abbreviations of the selected membranes can be observed in Table 3. From the technical data sheets of each selected membranes were provided test and operating information. These data are useful in our calculations concerning membrane permeability. In the following is presented the procedure and results of the membranes' permeability calculations.

For the whole range of membranes studied, the permeability was calculated with the equation [12]:

$$A = \frac{J}{\Delta P - \Delta \pi}; \tag{2}$$

where:

A – membrane permeability;

J – permeate flow (value takes from the technical data sheets of each selected membrane);

ΔP – permeate (working) pressure (value takes from the technical data sheets of each selected membrane);

Δπ – osmotic pressure (as arithmetic media from feed pressure and retentate pressure) calculated with the equation [12]:

$$\Delta\pi = \frac{RT \cdot \Delta c \cdot n}{M} \tag{3}$$

where:

R - universal ideal gas constant;

T - the temperature at which the permeate flow was obtained (from the technical sheet of each membrane) in K;

Δc - the salt concentration in the feed for which the permeate flow was obtained (from the technical sheet of each membrane);

n - the number of chemical elements (i.e. for NaCl, *n*=2);

M – molecular weight of the salt (i.e. M_{NaCl} =58.5 g/mol).

The results of membranes' permeability is in the range of 0.61 liter/m^2·h·bar to 1.87 liter/m^2·h·bar, as seen in Table 3.

Table 3. *Calculated permeability of selected membranes*

Commercial name of the membrane module	Permeability (liter/m^2 · h · bar)
Hydranautics SWC6 – LD	1.83
Koch TFC – HF – 8"	1.48
Toray TM820V – 400	1.36
Toray TM829L - 400	1.87

The selection of membranes according to the physico-chemical characteristics of seawater and the choice of operating pressure

In the following, for each selected membrane, the total area required in a RO plant, in order to obtain a permeate flow of 1 000 m^3/day and a salt concentration in the permeate of 225 ppm was calculated. The calculation of the required membrane area was done iteratively for a range of pressures keeping the feed temperature and concentration constant, for a range of feed flow concentrations at constant pressure and temperature, respectively for a series of temperatures at constant feed salt concentration and pressure. Thus, for this study the following operating conditions were selected:

- operating pressure in range of 35 bar to 65 bar (selection based on data information from technical sheets of membranes);
- operating temperature between 20°C to 50°C (selection based on data information from technical sheets of membranes);
- seawater salinity in RO feed in range of 30 000 ppm to 50 000 ppm according to data from Table 1 and Table 2.

Membrane area calculations were made for a simple single-stage plant without concentrate recirculation, as shown in Figure 4.

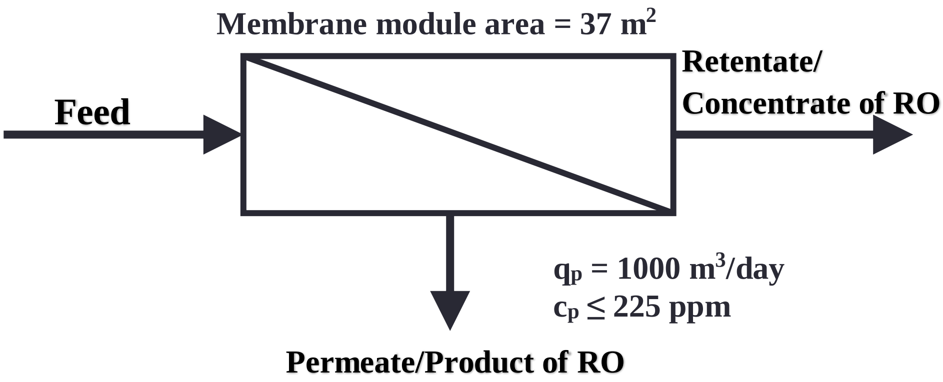

Figure 4. *Simplified flowsheet of a reverse osmosis unit.*

The algorithm for calculating the required total membrane area for a RO desalination plant was as follows [12]:

a) Salt concentration in retentat:

$$c_r = c_f (1 - S)^{-R} \text{ [ppm]} \tag{4}$$

where:

c_f – salt concentration in feed;

S – recovery rate (from the technical sheet of each membrane);

R – salt retention (from the technical sheet of each membrane).

b) Medium salt concentration of permeate:

$$\overline{c_p} = \frac{c_f}{S}\left[1 - (1 - S)^{1-R}\right] \text{ [ppm]} \tag{5}$$

c) Osmotic pressure of the feed (it is considered only NaCl):

$$\Delta\pi_f = \frac{R \cdot T \cdot c_f \cdot 2}{58.5} \text{ [bar]} \tag{6}$$

d) Osmotic pressure of retentate/concentrate (it is considered only NaCl):

$$\Delta\pi_r = \frac{R \cdot T \cdot c_r \cdot 2}{58.5} \text{ [bar]} \tag{7}$$

e) Medium osmotic pressure:

$$\Delta\pi = \frac{\Delta\pi_f + \Delta\pi_r}{2} \text{ [bar]} \tag{8}$$

f) Permeate flow:

$$J = A(P - \Delta\pi) \cdot 24 \text{ [liter / m}^2 \cdot \text{day]} \tag{9}$$

where: P – operating pressure.

g) Membrane area:

$$Area = \frac{q_p}{J} \; [\, \mathrm{m}^2 \,] \tag{10}$$

where: q_p - permeate flow [m^3 / day].

The results obtained after applying the algorithm for calculating the area of the selected membranes are presented below. Based on these results, the membrane area variations were graphically represented depending on the salt concentration in the feed stream, the operating pressure and the operating temperature of the reverse osmosis unit.

A. Calculation of the total membrane area for a RO desalination plant depending on the salt concentration in the feed, at:

- operating pressure = 55 bar;

- operating temperature = 25°C.

The obtained data can be seen in Figure 5.

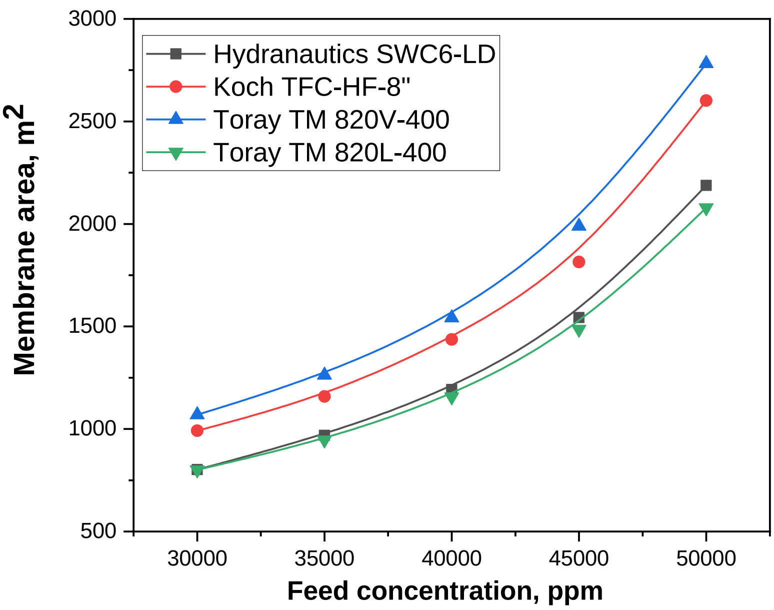

Figure 5. *The variation of the area of the membranes depending on the feed concentration.*

From Figure 5 it is observed that:

- with the increase in the salt concentration in the feed, the total membrane area of the RO system also increases, regardless of the membrane type (membrane permeability) in the RO process;

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- for an increase in the feed salt concentration from 30 000 ppm to 50 000 ppm, the total area of the RO system increases by 2.6 times for the membranes produced by the commercial companies Koch and Toray and by 2.73 times for the membranes produced by Hydranautics company;
- at a feed salt concentration, for example, at 35000 ppm, the total area of the RO system equipped with the Toray TM820L-400 membrane (permeability of 1.87 liters/m^2·h·bar) is 37% greater than in the case of a RO system equipped with the Toray TM829V - 400 membrane (permeability 1.36 liters / m^2 · h · bar).

B. Calculation of the total membrane area for a RO desalination plant depending on the operating pressure, at:

- salt concentration in feed= 35 000 ppm;

- operating temperature = 25°C.

The obtained data can be seen in Figure 6.

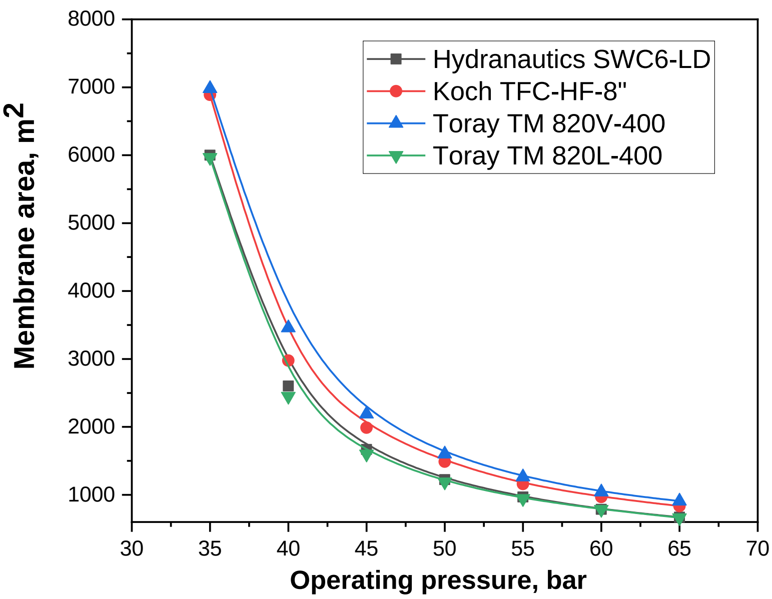

Figure 6. *The variation of the area of the membranes depending on the operating pressure.*

From Figure 6 it is observed that:

- a decrease in operating pressure, in the range of 45-50 bar, leads to a significant increase in the total membrane area of the RO system. Such an operating situation could be encountered where reduced energy consumption is desired (i.e., insular geographic areas without energy resources or restrictions imposed by environmental protection, etc.). In any other geographical area, it would be recommended to operate the RO system in the 50-55 bar pressure range, regardless of the type of membrane selected;

- an increase in operating pressure from 50 bar to 60 bar, would have a relatively modest response to the increase in the total membrane area of the RO system: for example, the total area of the RO system equipped with the Toray TM820L-400 membrane (permeability of 1.87 liters/ $m^2 \cdot h \cdot bar$) an increase of 1.51 times occurs, and for a system equipped with Hydranautics SWC6 – LD (permeability of 1.83 liters/$m^2 \cdot h \cdot bar$) the pressure increase is 1.55 times. However, a pressure increase of 10 bar in the feed stream could mean significant energy consumption. Only a detailed economic calculation (investment and operation) could decide the economy of the process.

C. Calculation of the total membrane area for a RO desalination plant depending on the temperature, at:

- salt concentration in feed 35 000 ppm;

- operating pressure = 55 bar.

The obtained data can be seen in Figure 7.

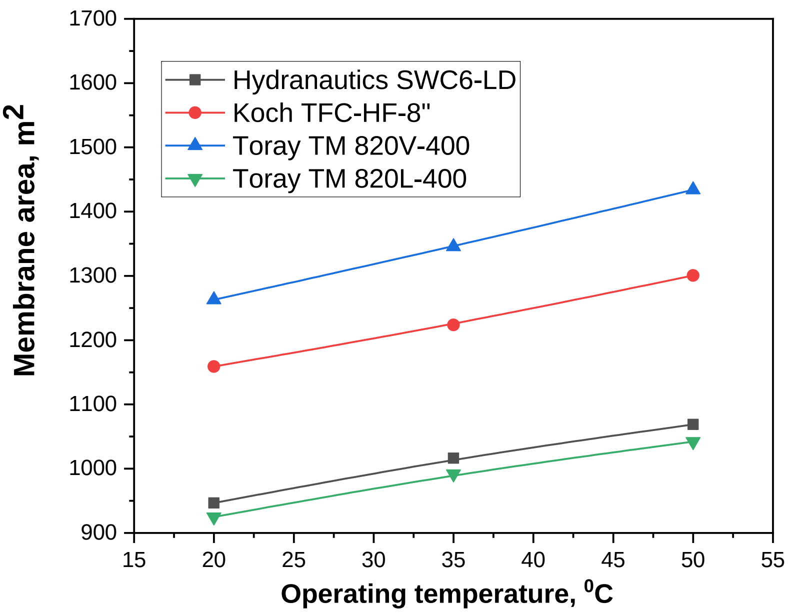

Figure 7. *The variation of the area of the membranes depending on the operating temperature.*

From Figure 7, it is observed that:

- an increase in operating temperature, in the range of 20-50˚C, leads to a significant increase in the total membrane area of the RO system, especially to the systems equipped with low permeability membranes (i.e., Koch TFC – HF – 8” and Toray TM820V – 400);

- regarding the behaviour of membranes with high permeabilities (i.e., Hydranautics SWC6 – LD and Toray TM829L – 400), both show a similar increase in area with increasing the operating temperature in the range of 20-50˚C, namely an increase of 1.13 times.

In the design of seawater desalination plants by RO, membrane permeability is an important characteristic, with a significant impact on both investment and operating costs, which must be considered, also related to the cost of the membrane per surface unit.

CONCLUSIONS

Water is a vital resource for all people on earth. But, it is equally important for economic and social development. The seawater desalination plants based on reverse osmosis are a major solution for solving the drinking water crisis.

In this work, it was shown that:

- by experimental determination, the salinity of the four samples of seawater taken from the Mediterranean basin, namely Paralia Katerini - Greece, Civitavecchia - Italy and Tunis - Tunisia and a large water sample from the Persian Gulf (Manifah - Saudi Arabia) demonstrated that the salinity (expressed as "total dissolved ions") is 38-39 g/l (see Table 2). These values fall within the range of those reported in the literature (see Table 1). Regarding, the experimental value of the salinity of the water sample taken from the Persian Gulf (i.e. Manifah - Saudi Arabia), it is 50.5 g/l, and also this value is in accordance with that reported in the literature (i.e. 39 - 52 g /l);
- to start designing a seawater desalination plant based on membrane reverse osmosis process, the first step is the selection of the membranes. The primary criterion is their permeability. Among the membranes marketed by companies dedicated to seawater desalination through reverse osmosis, four types of membranes were selected for our study that may correspond to the purpose of our design: a permeate flow J of 1000 m^3/day and a salt concentration in the permeate of 225 ppm and for an area of the standard membrane module of 37 m^2. According to eqs. (2 and 3), also respecting the technical sheets of the membranes selected for the study, the results of our calculation showed that the Hydranautics SWC6 – LD and Toray TM829L - 400 membranes resulted in permeabilities of over 1.8 liters/m^2·h·bar, and the Koch membranes TFC - HF - 8" and Toray TM820V - 400 have permeabilities around 1.4 liter/m^2·h·bar (according to Table 3).

In the next step of our study of seawater desalination by reverse osmosis, based on the permeability values of the four types of membranes, the influence of the operating pressure, operating temperature and the seawater salinity in RO feed was studied, over the total area of a RO desalination plant.

From our study, it is clear that the selection of membranes with high permeability leads to significant benefits on the total area (and implicitly on the investment cost) of the RO system. The concentration of salts in the feed and the operating pressure have the most significant influence on the increase in the total area of the membranes in the reverse osmosis installation. However, the operating parameters (pressure and temperature) have a strong dependence with the geographical position of the desalination plant.

So, no desalination plant can closely resemble another. The final decision can only be based on an extensive technical-economic study, particularly for each geographical location of the reverse osmosis desalination plant.

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