Performance evaluation and boron rejection in a SWRO system under variable operating conditions

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1. Introduction

Boron is an important nutrient, especially for plant growth (Darwish et al., 2020). The margin between a deficient and a toxic concentration of boron is very small and the regulations in this respect are therefore usually quite restrictive (Ruiz-García et al., 2019). Usually, boron concentration in seawater is around 5 ppm and is in the form of boric acid (H₃BO₃) (Hilal et al., 2011). This is an uncharged weak acid and the separation of species by reverse osmosis (RO) membranes depends mainly on their charge (Qasim et al., 2019). As a result, boron rejection is a major concern in seawater reverse osmosis (SWRO) desalination plants (Cengeloglu et al., 2008; Koseoglu et al., 2008b). Considerable efforts have been made to make new RO membranes that increase boron rejection (Li et al., 2020; Jung et al., 2020). Another well-developed research line is related to proposals for alternative processes to RO that separate boron from aqueous solutions or seawater (Wolska and Bryjak, 2013; Najid et al., 2021). These processes include adsorption (Kluczka et al., 2019), adsorption-membrane filtration (Darwish et al., 2017), electrocoagulation (Chen et al., 2020), electrodistillation (Jarma et al., 2021), hybrid FO-RO processes (Ban et al., 2019), membrane distillation (Alkhudhiri et al., 2020; Ozbey-Unal et al., 2018), forward osmosis (FO) (Darwish et al., 2020), ion exchange resins (Hussain et al., 2019), polymer-enhanced ultrafiltration (Neo et al., 2019), and continuous electrodeionization (Jiang et al., 2018). Although SWRO desalination technology is able to produce permeate water with appropriate boron concentrations, there is a high degree of dependency on a number of factors, including the membrane boron permeability coefficient (Bₚ) (Wang et al., 2018), operating conditions (Hyung and Kim, 2006; Sagiv and Semiat, 2004) and the fouling effect during the operating time that can produce an increase in Bₚ (Ruiz-García et al., 2019). This question becomes more challenging when an RO desalination plant is forced to operate under variable operating conditions (Ruiz-García et al., 2020).

The challenge to reduce boron concentration in the permeate produced by SWRO desalination plants has been studied extensively by the scientific community (Farhat et al., 2013). This is an
The intensive use of energy in SWRO desalination plants has promoted the use of renewable energy sources (RES) to provide the power for this technology (Nassrullah et al., 2020). The application of RES to power SWRO is not simple, and its viability depends on many factors such as water and energy accessibility (Nassrullah et al., 2020), costs (Elmaadawy et al., 2020; Rezk et al., 2020), regulations (Sen and Ganguly, 2017), etc. There are two main factors in the operation of an SWRO desalination plant, permeate production and permeate quality in terms of total dissolved solids (TDS). Both factors are affected when an off-grid RES is powering the SWRO system under variable conditions. de la Nuez Pestana et al. (2004) studied the variable operation of an SWRO system directly connected to a wind turbine without any energy storage system. The membrane installed in this SWRO system was the TFC 2822-3S from Koch Fluid Systems™, and actual seawater (as opposed to synthesized) was used. The feed pressures (p_f) applied were 39, 49 and 60 bar, with flux recoveries of 19.74, 31.37 and 40% respectively. Permeate conductivity was between 429 and 292 μS cm⁻¹, with lower values at pressures of 49 and 60 bar. Ntavou et al. (2016) carried out a performance analysis of a multi-skid SWRO unit under variable power input. They used a FILMTEC™SW30-4040 membrane and a synthesized feed solution by adding salt to tap water to reach 37,500 ppm. It was observed that the lower the TDS in the permeate (TDS_p) the higher the power input that was required, with TDS_p ranging between approximately 150 and 250 ppm. Dimitriou et al. (2017) validated a theoretical model for predicting SWRO systems under variable operating conditions. As in the previous study, the membrane used was the FILMTEC™SW30-4040 in a small-scale SWRO unit with one pressure vessel (PV) and a Clark pump unit. p_f ranged between 35 and 45 bar approximately and TDS_p between 200 and 600 ppm. They also obtained lower TDS_p with higher p_f. The same SWRO system was used by C.-S. Karavas et al. (2018), incorporating a short-term energy storage system. In this case, they operated the SWRO system in a p_f range of between 39 and 51 bar, with a permeate conductivity of between 200 and 1000 μS cm⁻¹. As is usual in these desalination systems, the higher the power input was, the higher the pressure and R and the lower the TDS_p were. Calise et al. (2019) carried out an economic assessment study of SWRO desalination powered by photovoltaic panels. The performance analysis of the SWRO system was based on a simulation using the Water Application Value Engine (WAVE) software from Dupont® and a model proposed by the authors which showed similar results. The performance was assessed in terms of R and salt rejection. An off-grid solar energy system to power an SWRO desalination plant with integrated photovoltaic thermal cooling was proposed by Monjezi et al. (2020). The modeling and operation of the SWRO system was simulated with the Reverse Osmosis System Analysis (ROSA) software. The authors studied the Filmtec™SW30-2540 membrane, working with a single stage.
with an $R$ of 40%. An inorganic feedwater was used as input, but boron concentration was non-existent and the concentration of each ion in the permeate was estimated by the software. Delgado-Torres et al. (2020) undertook a preliminary study of an SWRO process powered by a hybrid system (photovoltaic - tidal range). The performance of the SWRO system was simulated with ROSA, considering two SWRO membranes: FILMTEC™SW30HRLE - 440i and FILMTEC™SW30XLE - 440i. The inorganic composition of the feedwater was not detailed and only the TDS of one operating point for each membrane was shown. Unfortunately, the issue of boron rejection in SWRO systems working under variable operating conditions has not been extensively studied. The permitted boron concentrations according to different regulations are low. While the World Health Organization (WHO) established a maximum boron concentration of 2.4 ppm for drinking water in 2011, the EU limit is just 1.0 ppm. This limiting factor can reduce the safe operation windows (SOWs) of SWRO systems working under variable input power as supplied by RES.

The aim and novel contribution of this paper is the evaluation of the performance and the boron rejection under variable operating conditions of two commercial SWRO membranes (TM820L-440 and TM820S-400 from Toray) in full-scale PVs. To carry out this work, a simulation algorithm previously validated and published by the authors Ruiz-García and de la Nuez-Pestana (2018) was adapted to estimate the behavior of a single-stage SWRO system with the aforementioned membranes installed. The permeability coefficients of RO membranes are characteristic to each membrane and show membrane efficiency in terms of water production and solute rejection. The initial average water, salt and boron permeability coefficients that were used were taken from a previous published work (Ruiz-García et al., 2019).

2. Material and methods

2.1. Permeability coefficients

Determination of the initial water permeability coefficient ($A$), salt permeability coefficient ($B_s$) and $B_B$ was carried out using the experimental data of the initial operating point of a full-scale SWRO desalination plant with TM820L-440 and TM820S-400 membranes installed. A more detailed description of this desalination plant can be found in a previous work published by one of the authors Ruiz-García et al. (2019). More specifically, the initial data of trains 2 (TM820L-440) and 9 (TM820S-400) were used. These trains were selected as their initial operating time was closer to 0 than the other trains and so their membranes were the least used. The number of PVs was 90 and 79 for trains 2 and 9, respectively. Each PV had 7 SWRO membrane elements in series (Fig. 1). As the operating data were usually collected at the input and output of the PVs, this allowed calculation of the average permeability coefficients. The detailed procedure for calculating the permeability coefficient can be found in a previous study by Ruiz-García et al. (2019). Conductivity was measured using a Hanna Instruments EC 215 conductivity meter, and boron concentration in the permeate was determined using the carmine method. The pH was close to 7, so $B_B$ was calculated as boric acid. The permeability coefficients per SWRO membrane module were estimated from the initial operating data. Table 1 shows the dimensional characteristics and performance under manufacturer test conditions ($p_t=5.52$ MPa, feed-brine temperature ($T_{fb}$) =25 °C, $C_t=32,000$ ppm NaCl, $R=8\%$, $pH_p=8$ and 5 ppm boron added to feedwater) of the SWRO membranes and Table 2 shows the initial operating values per PV and the permeability coefficients for each membrane. For these calculation the Equations of Table 3 were used.

2.2. Process modeling

The simulation algorithm (Ruiz-García and de la Nuez-Pestana, 2018) used the solution-diffusion (Qasim et al., 2019; Al-Obaidi et al., 2017) transport model. This is the most commonly used model for simulating (Joseph and Damodaran, 2019) and predicting RO system performances (Alsarayreh et al., 2020a; Al-Obaidi et al., 2019) as usually provides results close to the real behavior of these systems, despite its limitations (Alsarayreh et al., 2020b). The transport equations are applied for each membrane element considering averages. The temperature $T$ and pressure drop in the permeate along the RO system were disregarded. More details about the simulation algorithm can be found in a previous work (Ruiz-García and de la Nuez-Pestana, 2018). A fouling factor ($FF$) of 1 was considered (new membrane) along with a $T_{fb}$ of 25 °C, and so the temperature correction factor ($TCF$) was 1. $5_m$ is the active membrane surface, NDP the net driving pressure, $I$ the membrane length, $v_{fb}$ the feed-brine velocity, $\varepsilon$ the porosity in the feed-brine channel (considered 0.89 for both membranes), $h$ the feed-brine spacer height (28 milli-inches = $7.11 \times 10^{-4}$ m), $PF$ the polarization factor, $k_s$ the solute mass transfer coefficient and $\eta$ the dynamic viscosity of water (0.0008891 kg m$^{-1}$ s$^{-1}$). To determine all the above variables, the aforementioned algorithm was imple-
mented in MATLAB®. The results are presented per PV of 7 membrane elements each (as in the actual SWRO system). The simulations were carried out with the following operating ranges per PV: $Q_i$ from 5 to 16 m$^3$ h$^{-1}$ since for $Q_i$ between 5 and 5 m$^3$ h$^{-1}$ the operating window was small and with low $R$, $Q_i$ from 32 to 45 g L$^{-1}$ and $p_i$ from 4 to 7 MPa. Boron concentration in the feedwater was considered as 5 ppm in all cases in accordance with the analysis of the feedwater carried out in the desalination plant (Ruiz-Garcia et al., 2019). Only NaCl was increased. The specific energy consumption (SEC) was determined considering the ideal performance of the high pressure pump (100% efficiency for the electrical engine and pump). No energy recovery devices were considered in the simulations.

### Table 2
Operating parameters and SWRO membrane permeability coefficients.

| Parameters                  | TM820L-440 | TM820S-400 |
|-----------------------------|------------|------------|
| Feed flow ($Q_i$) (m$^3$ h$^{-1}$) | 8.53       | 9.7        |
| Feed pressure ($p_i$) (MPa)    | 6.7        | 6.45       |
| Permeate flow ($Q_p$) (m$^3$ h$^{-1}$) | 3.83       | 4.28       |
| Permeate concentration ($c_p$) (ppm) | 251.44     | 240.8      |
| Boron concentration in the permeate ($c_{p,B}$) (ppm) | 0.6        | 0.89       |
| Initial average water permeability coefficient ($A_w$) (m Pa$^{-1}$ s$^{-1}$) | $1.24 \times 10^{-12}$ | $2.01 \times 10^{-12}$ |
| Initial average solute permeability coefficient ($B_{av,s}$) (m s$^{-1}$) | $1.76 \times 10^{-8}$ | $2.20 \times 10^{-8}$ |
| Initial average boron permeability coefficient ($B_{av,B}$) (m s$^{-1}$) | $3.55 \times 10^{-7}$ | $7.31 \times 10^{-7}$ |
| Initial $A$ ($m$ Pa$^{-1}$ s$^{-1}$) | $1.85 \times 10^{-12}$ | $2.65 \times 10^{-12}$ |
| Initial $B_s$ (m s$^{-1}$) | $1.55 \times 10^{-9}$ | $1.75 \times 10^{-9}$ |
| Initial $B_B$ (m s$^{-1}$) | $3.15 \times 10^{-7}$ | $5.65 \times 10^{-7}$ |

### Table 3
Transport equations.

#### Permeate flow
$$Q_p = A \cdot NDP \cdot S_m$$  
#### Water permeability coefficient
$$A = A_0 \cdot TCP \cdot FF$$  
#### Net driving pressure
$$NDP = (\Delta p - \Delta \pi) = p_i - p_f - \pi_m + \pi_p$$  
#### Friction factor
$$\lambda = 2.3Re^{-0.2}$$  
#### Reynolds number
$$Re = \frac{Q_i \cdot D}{\nu}$$  
#### Hydraulic diameter
$$d_h = \frac{4Q_i}{\pi \cdot D}$$  
#### Seawater density
$$\rho_{sw} = 1024.3 + 10.1 \cdot 0.0005 \cdot \sqrt{T}$$  
#### Empirical parameter
$$M = 1.0009 \cdot 2.757 \times 10^{-4} \cdot T_b$$  
#### Feed-brine concentration
$$C_{fb} = C_f \left( \frac{\sqrt{Q_i}}{\sqrt{T}} \right)$$  
#### Osmotic pressure
$$\pi = 4.54047 \left( 10^3 \cdot C/(\rho \cdot \eta) \right)^{0.867}$$  
#### Concentration on membrane surface
$$C_m = C_{fb} \cdot FF$$  
#### Polarization factor
$$PF = \frac{C_f}{C_{fb}} = \phi^\delta$$  
#### Shearwood number
$$Sh = 0.14 \cdot Re^{0.64} \cdot Sc^{0.42} \cdot \frac{D}{h_f}$$  
#### Schmidt number
$$Sc = \frac{\nu}{D}$$  
#### Boron mass transfer coefficient (Tanguchi et al., 2001)
$$B_{m,B} = \frac{0.72598 \cdot 0.023087T_b + 0.00027657T_b}{7.2}$$  
#### Solute diffusivity
$$D_s = \frac{0.72598 \cdot 0.023087T_b + 0.00027657T_b}{7.2}$$  
#### Permeate concentration
$$C_p = B \cdot FF \cdot TCP \cdot \frac{C_f}{C_{fb}}$$  
#### Concentration factor
$$CF = \frac{Q_i}{Q_p}$$  
#### Flux recovery
$$R = \frac{100}{\eta}$$  
#### Rejection
$$Rejection = 100 - \frac{C_f}{C_{fb}}$$

3. Results and discussion

The results shown in Figs. 2–9 were obtained considering $C_f$=35,000 ppm. Figs. 2 and 3 show the $R$ of the TM820L-440 and TM820S-400 membranes, respectively. It can be observed that higher $R$ was achieved with the TM820S-400 membrane for the same operating points. The influence of coefficient $A$ was higher than the active area of the membranes in terms of $R$. High $R$ values can bring some membrane elements close to thresholds imposed by manufacturers including, for example, $R$ higher than 15% per element or brine flow rates ($Q_p$) very close to 3 m h$^{-1}$. Such operating conditions can decrease notably the system performance over long periods of operation and mean that more frequent chemical cleanings are required, etc. The highest $R$ values obtained were 57.56 and 58.45% for the TM820L-440 (7 MPa, 7.25 m$^3$ h$^{-1}$) and TM820S-400 (7 MPa, 8.5 m$^3$ h$^{-1}$) membranes, respectively.

Figs. 4 and 5 show the SEC values of the TM820L-440 and TM820S-400 membranes, respectively. As usual, the membrane with higher $R$ had the lower SEC. The TM820L-440 membrane had a larger SOW, mainly due to the $A$ coefficient. This membrane had lower production, and so there were more operating points where restrictions such as minimum $Q_p$ or maximum $R$ per membrane element were not reached. For this reason, depending on the operating conditions, it is not advisable to have many high production membrane elements in series. Minimum values of SEC were 3.12
Fig. 3. R (%) of the membranes TM820S-400.

Fig. 4. SEC (kWh m\(^{-3}\)) of the membranes TM820L-440.

Fig. 5. SEC (kWh m\(^{-3}\)) of the membranes TM820S-400.

Fig. 6. \(C_p \times 10^{-3}\) (ppm) of the membrane TM820L-440.

Fig. 7. \(C_p \times 10^{-3}\) (ppm) of the membrane TM820S-400.

Fig. 8. \(C_{pB}\) (ppm) of the membrane TM820L-440.

Fig. 9. \(C_{pB}\) (ppm) of the membrane TM820S-400.

and 3.27 kWh m\(^{-3}\) for membranes TM820S-400 and TM820L-440 respectively (considering ideal performance). Usually these operating points are very close to the thresholds imposed by manufacturers and it is convenient to take safety margins in real operation. The lowest SEC values obtained were 3.2683 and 3.1180 kWh m\(^{-3}\) for the TM820L-440 (5.85 MPa, 6 m\(^3\) h\(^{-1}\)) and TM820S-400 (5.55 MPa, 6 m\(^3\) h\(^{-1}\)) membranes, respectively.

For both membranes, the higher \(Q_f\) and \(p_f\) were the lower \(C_p\) was (Figs. 6 and 7). The higher \(Q_p\) and the lower \(CF\) were, the lower \(C_p\) was (Eq. (17)). High values of \(Q_p\) required high values of \(Q_f\) and \(p_f\). The mentioned two figures show the role of coefficient \(B\) in solute rejection. The difference is very small as the coefficients are quite close \((1.55 \times 10^{-8} \text{ vs } 1.75 \times 10^{-8})\). It should be considered that fouling could have a different impact on both membranes making the coefficient \(B\) vary differently. However, the difference between the two membranes in terms of \(B_p\) was more pronounced. This can be observed in Figs. 8 and 9, which show
In actual operation, fouling can cause the permeability coefficients to change (Ruiz-García and Nuez, 2020), in which case all the possible operating points would be displaced with respect to the calculated ones. A decrease in coefficient $A$ can produce decreases in $R$ and/or increases in SEC if a constant $R$ is desired by increasing $p_f$. A change in coefficient $B_f$ could be delicate as it may result in the need for changes in the operating conditions to ensure the quality criteria are met, as well as, in some cases, premature membrane replacement.

### 4. Conclusions

An evaluation was undertaken in this work of boron rejection (in the form of boric acid) of two commercial membranes (TM820L-440 and TM820S-400) under variable operating conditions. The results show that the TM820L-440 membrane is the more suitable option in SWRO systems where the required $C_{5}$ is low (<1 ppm) and a priority. However, as the TM820L-440 requires more energy than the TM820S-400, the latter is more appropriate when $C_{5}$ is not a priority or when the limiting concentration is not very low, such as for agricultural purposes (non-boron-sensitive crops). It should be noted that this was a static study (constant permeability coefficient) and that in SWRO systems the permeability coefficient is usually not constant, mainly due to the effect of fouling on the system. This can produce important variations in performance and may require changes to the operating conditions. Works on the sizing and techno-economic assessment of RES-powered SWRO systems should take into account not only the SOW, considering new membranes or constant permeability coefficients, but also the change of these coefficients and its impact on the entire plant. The decrease in coefficient $A$ could result in lower permeate production or the need to oversize the RES system to provide the energy required to ensure constant long-term permeate production. Future works should consider different permeability coefficients under variable operating conditions to enable the determination of the most suitable membranes in terms of performance in certain operating ranges.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### CRediT authorship contribution statement

**A. Ruiz-García**: Conceptualization, Methodology, Data curation, Writing - original draft, Visualization, Investigation, Validation, Writing - review & editing. **I. Nuez**: Conceptualization, Resources, Supervision.

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