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Rebuttal to “Discussion of ‘Second law analysis of reverse osmosis desalination plants: an alternative design using pressure retarded osmosis’ [Energy (2011) 36: 6617-6626]”

Introduction
We have had several conversations with Knutson during recent months, and we certainly agree that the one-dimensional mass exchanger model is more appropriate than the zero-dimensional model which has appeared in much of the past literature and which we also applied. We have been working on revisions of these calculations that incorporate the one-dimensional model, and we report some of our findings in the following (Banchik and Lienhard V, 2012; Sharqawy et al., 2012). However, we believe that PRO has clear potential for energy recovery, as we explain in detail below. Further, Knutson’s analysis of the power generation is flawed and his conclusions regarding energy recovery are not accurate.

Knutson’s method of analysis makes the assumption of infinite membrane water permeability (equivalent to infinite surface area), taking the value of A in Eq. (1) to be infinity. Because the value of A for the membrane is assumed to be infinite, the local water flux is equal to zero at the inlet, outlet, or both ends of the PRO module. In another words, the driving force for the water flux will vanish at the inlet, outlet, or both ends. This is similar to the assumption of zero pinch at the end of a heat exchanger, such as might be obtained with infinite surface area. This is an interesting method, and it should give similar trends as obtained given in (Sharqawy et al., 2011) if it is applied correctly.

It is important to note that (Sharqawy et al., 2011) used an exergy analysis method in which the membrane characteristic A was increased continuously until reaching a point at which the entropy generation is zero. After this point the entropy generation is negative which violates the second law of thermodynamics as discussed in the paper. However, an incorrect value for the osmotic pressure at low salinity was used in that analysis, and consequently some of the values given in Table 3 in (Sharqawy et al., 2011) are incorrect. In addition, the values on the axes of Figure 9 and 10 in that paper are also incorrect. However the trend and the main conclusion are unchanged. In the next section, we give the correct solution, using Knutson’s assumption of infinite A, after explaining his miscalculation of the energy recovery. In addition, we give the corrected values for Table 3 in (Sharqawy et al., 2011) and Figures 9 and 10. It is important to mention here that many authors have presented similar ideas regarding the energy recovery of the brine disposed from desalination plants (Ahmad and Williams, 2009) and in particular from RO desalination plants (Martinetti et al., 2009).
Correction of Knutson Method

In this section, we use the same assumptions made by Knutson and present the correct energy generation values. Equation (2) used by Knutson \( W_{\text{PRO}} = Q \Delta P \), where \( \Delta P \) is the average hydraulic pressure gradient) to calculate the energy generated from the PRO model is correct; however, the pressure difference used in the calculation leads to very low energy generation. This equation is appropriate for a stand-alone PRO system in which the draw solution (rejected brine) must be pressurized first before introducing it to the PRO module. In that case, Eq. (2) will calculate the net power produced by the PRO module. However, when using the rejected brine from an RO module to recover energy from the PRO module, the rejected brine is already at high pressure, and therefore the energy needed to pressurize the draw solution is saved. Thus, the energy generated by the PRO module in the case of pressurized draw solution is

\[
W_{\text{PRO}} = Q \Delta P + Q_{\text{brine}} (P_{\text{brine}} - P_{\text{atm}}),
\]

where \( Q \) is the total flow rate of water across the membrane, \( \Delta P \) is the average hydraulic pressure gradient, \( Q_{\text{brine}} \) is the flow rate of the draw solution (rejected brine from the RO module), \( P_{\text{brine}} \) is the pressure of the draw solution, and \( P_{\text{atm}} \) is the atmospheric pressure. This assumes that all high pressure streams from the PRO module will expand to atmospheric pressure using hydraulic turbines of 100% efficiency similar to Knutson’s assumptions as well as those of (Sharqawy et al., 2011). It is important to notice that the second part of Eq. (1) is the energy that can be recovered from the RO module using just a hydraulic turbine (or pressure exchanger) directly expanding the pressurized brine to atmospheric pressure. The first part of Eq. (1) represents the extra energy that can be recovered when a PRO module is used. The summation of the two parts in Eq. (1) is the total energy produced from the PRO module. In Knutson’s calculations, the second right-hand side term in Eq. (1) has been ignored and therefore, the energy produced from the PRO system given in Knutson’s Figure 2 is too low. The correct values are given in Figure 1.
Equation (1) clearly shows that using a PRO-RO system has advantages compared with using only a hydraulic turbine or pressure exchanger to recover energy from the pressurized brine rejected from the RO plant. The particular RO plant considered here uses brackish water, and so the salinity of the rejected brine is very low ($w_c = 6.11 \text{ g/kg}$) compared with the salinity of the rejected brine from a seawater RO plant (SWRO). This reduces the amount of water that can permeate through a PRO module and hence reduces the energy produced. In this case, the energy recovery by adding the PRO module is about 11% (3 kW) from the energy recovered from the pressurized rejected brine alone (28 kW). For a SWRO system, the recovered energy is estimated to be 50% (assuming the rejected brine has a salinity of 70 g/kg and 10 bar pressure, the feed solution is of 35 g/kg salinity, and using Knutson’s assumptions with $A \rightarrow \infty$).
Correction of Sharqawy et al., 2011 Results

(Sharqawy et al., 2011) used an exergy analysis method to calculate the maximum power that can be recovered from the rejected brine of the RO plant using a PRO unit. In that paper, the membrane characteristic, A, was increased continuously until reaching a point at which the entropy generation is zero. After this point the entropy generation is negative, which violates the second law of thermodynamics, as discussed in that work. The water flux through the membrane was calculated using a zero-dimensional model in which the inlet conditions of the feed and draw streams were used in the calculations of the water flux that permeates through the membrane. This is effectively a system with infinite quantities of both feed and draw solutions, so that bulk salt concentrations are fixed, which results in a very large amount of water flux through the PRO membrane.

We have applied a one-dimensional model in which the osmotic pressure gradient is taken into consideration to recalculate the results of the previous paper. At any assumed membrane characteristics the total water flow (accumulated over the entire membrane area) through the PRO module reaches a maximum value whenever at any point the local osmotic pressure difference is equal to the local pressure difference. At this condition, the entropy generation is not zero; however it has the lowest positive value, as shown in the corrected Figure 9. In addition, the second law efficiency is increasing until the same condition is reached, as is also shown in the figure. The trend of both old Figure 9 in (Sharqawy et al., 2011) and the corrected one are the same. However, the point at which the limit of A is reached is not zero entropy generation because this process is an irreversible process under the one-dimensional model. In this irreversible case, the limit of A is reached when the local driving force for the water flux permeating through the PRO membrane is reached. These results are in agreement with Knutson’s findings. A modified version of Table 3 of (Sharqawy et al., 2011) is shown below in which the corrected values of states 11 – 16 are in bold. It is noticed that the rejected brine (state 6) is diluted to a salinity of 2.462 g/kg (state 11) which is disposed at much lower salinity (state 14). In addition, row water (state 15) is mixed with RO permeate to meet the target salinity (0.23 g/kg) and quantity of product water (state 8).

The corrected Figure 10 below shows the reduction in the input work for the whole modified RO plant. It is important to note here that the increase in the second law efficiency and the reduction in the input work are not very substantial because the salinity of the rejected brine is very low in the brackish water RO plant studied (BWRO). However, as mentioned earlier, the energy recovery gain is estimated to be 50% larger than what would be obtain using only a hydraulic turbine or pressure exchanger to recover the energy from the pressurized rejected brine. In this case, a more accurate one-dimensional model together with a system optimization computation are required to accurately calculate the work recovered. In addition, other effects such as concentration polarization, salt rejection, and pressure drop should be considered. We have been working on such studies, and we report some of our findings in (Banchik and Lienhard V, 2012; Sharqawy et al., 2012).
Corrected Table 3: Thermodynamic properties at various locations for the modified RO plant (changes from old solution are in bold)

| #  | $P$, kPa | $T$, °C | $w_s$, g/kg | $\dot{m}$, kg/s | $h$, kJ/kg | $e_f$, kJ/kg |
|----|---------|--------|-------------|----------------|------------|-------------|
| 0  | 101.3   | 15.0   | 1.550       | 100.70         | 62.93      | 0.0000      |
| 1  | 384.0   | 15.0   | 1.550       | 100.70         | 63.22      | 0.2825      |
| 2  | 370.2   | 15.0   | 1.550       | 100.70         | 63.20      | 0.2687      |
| 3  | 356.4   | 15.0   | 1.550       | 100.70         | 63.19      | 0.2550      |
| 4  | 1687.0  | 15.0   | 1.550       | 100.70         | 64.52      | 1.5849      |
| 5  | 101.3   | 15.0   | 0.020       | 75.37          | 63.06      | 0.0090      |
| 6  | 1225    | 15.0   | 6.110       | 25.29          | 63.67      | 1.1957      |
| 7  | 101.3   | 15.0   | 0.230       | 87.36          | 63.05      | 0.0067      |
| 8  | 101.3   | 15.0   | 0.230       | 87.36          | 63.05      | 0.0067      |
| 9  | 101.3   | 15.0   | 1.550       | 627.90         | 62.93      | 0.0000      |
| 10 | 1161    | 15.0   | 1.550       | 627.90         | 63.99      | 1.0599      |
| 11 | 1225    | 15.0   | 2.462       | 62.76          | 64.09      | 1.1260      |
| 12 | 1161    | 15.0   | 1.648       | 590.40         | 64.03      | 1.0595      |
| 13 | 101.3   | 15.0   | 2.462       | 62.76          | 63.01      | 0.0031      |
| 14 | 101.3   | 15.0   | 2.462       | 62.76          | 63.01      | 0.0031      |
| 15 | 101.3   | 15.0   | 1.550       | 11.99          | 63.01      | 0.0000      |
| 16 | 101.3   | 15.0   | 1.648       | 590.40         | 63.01      | 0.000004    |
Corrected Fig. 9: Second law efficiency and the entropy generation of the proposed RO desalination alternative design.
Corrected Fig. 10: The net input power of the proposed RO desalination alternative design.
References

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