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A Comparison of Prevalent Desalination Exergy Models

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ABSTRACT

The efficient use of energy resources is vital to mitigate environmental impacts such as climate change, and to reduce operating costs. Exergy analysis is widely accepted as a powerful analytical tool for energy systems, quantifying system and component irreversibilities, and acting as a focus for improvement opportunities. Several research groups have applied exergy analyses in the study of various desalination systems, including co-generation Multi-Stage Flash (MSF) and Reverse Osmosis (RO) systems. However, according to the literature, several exergy model variations have been used by these different researchers. The models differ on several levels; the equations used to calculate the specific exergy values, the model chosen to represent feed water constituency, and the choice of the salinity dead state definition. For those seeking to apply exergy analysis, this presents a serious challenge. How does one know which exergy model to use? Do the various models give similar results? Does the choice of dead state affect results significantly? The objective of this paper is to investigate these questions for two particular, widely used, exergy models. A dataset in the literature was used as the basis for comparison; the results show some interesting discrepancies, particularly in the key separation processes, nanofiltration (NF) and reverse osmosis systems. The exergy destruction terms calculated by the two models for the NF process differed by 23.6%; the difference was even more pronounced in the RO process, a 29.8% difference in the result obtained. An investigation into the choice of salinity dead state showed that the choice of dead state did not have a significant effect on the exergy destruction terms.

INTRODUCTION

Ensuring continued access to sufficient water and energy supplies, is perhaps, this century's most pressing economic issue. The two are inextricably linked, energy is required to purify water for potable and industrial uses, and water is used in power generation applications. Desalination, although initially, an energy intensive process, has lowered its energy footprint significantly in the last two decades. One important contributor to lower energy requirements has been a move from thermal desalination processes such as Multi-Stage Flash (MSF) to membrane processes such as Reverse Osmosis (RO). Not only has the change in purification process choice led to lower energy consumption, but the reverse osmosis process itself has seen its energy footprint decrease from a specific energy intensity of approximately 20kWh/m3 of product water in the 1970s, to less than 2kWh/m³ by 2004 [1]. According to recent reports, a value of 1.58kWh/m³ has been achieved under ideal conditions (new membrane, low water flux at 42% recovery) [2, 3]. Some of the main reasons for these energy efficiencies can be attributed to improved membranes, lower specific energy requirements as a result of higher flux [1, 4]; pump and motor efficiency improvements and the use of variable speed drives (VSDs) [1, 5]; and the implementation of energy recovery devices to harness wasted throttling valve energy [1, 3, 6-8]. Suitable pre-treatment and post-treatment of RO has increased global recovery rates, including the integration of technologies such as membrane distillation, microfiltration (MF) and nanofiltration (NF) [9-13].

One important method, which has been used by several research groups for the characterisation and optimisation of RO desalination plants, is exergy analysis [9, 11-20]. Exergy is a thermodynamic property, combining the First and Second Laws of thermodynamics, which determines that energy must not only be thought of in terms of quantity, but also, importantly, in terms of quality. Energy is always conserved in systems; exergy is not conserved but is destroyed due to thermodynamic irreversibilities. Exergy has been described as a powerful tool for energy system analysis [21-23]. However, for those undertaking an exergy analysis of desalination systems, there is a key challenge, several exergy desalination models exist. How

does one know which exergy model to use, and do these models give similar results?

This paper seeks to compare two prevalent exergy RO desalination models; the paper can be broken down into four sections, (1) an overview of the two exergy models, (2) development of a means of comparing the two exergy models, (3) results of the model comparison (4) initial evaluation of the dead state influence.

NOMENCLATURE

Acronyms

RO	Reverse Osmosis	
MSF	Multi-Stage Flash	
NF	Nanofiltration	
MF	Microfiltration	
VSD	Variable Speed Drive	
TV	Throttling Valve	
TDS	Total Dissolved Solids	

1 7		Tillotting valve
TDS		Total Dissolved Solids
Syml	ools	
Ex	kW or KJ/hr	Exergy rate
'n	kg/s or kg/hr	Mass flow rate
h	KJ/kg	Specific enthalpy
T	K	Temperature
S	KJ/kgK	Specific entropy
R	KJ/Kmol K	Universal gas constant
R_{im}	KJ/Kmol K	Specific gas constant of the ideal mixture
c_p	K.J/kgK	Specific heat capacity
P	Pa or bar	Pressure
ρ	kg/m ³	Density
N	Kmol/kg	Number of moles per unit mass
x_l	%	Mole fraction of solvent (water)
c	mg/l	Concentration
MW	Kmol/kg	Molar mass (molecular weight)
mf	% or ppm	Mass fraction
1000	# (# cond)	and a second second

Subscripts and superscripts

Dead State	
Component under consideration	
Salt	
Water	
Solvent	
At the relevant process stage	
At the dead state	
Ideal mixture	
Concentration	
Pressure	
Temperature	

OVERVIEW OF THE TWO MODELS

For RO and other membrane separation systems, the majority of exergy analyses reported in the desalination literature are carried out using either one of two models. In order to differentiate them, the two models are termed, Model A and Model B. There are key differences between the two models; (1) the equations used to calculate the specific exergy at the relevant process stages, (2) the modelling of saline solution constituents and (3) the dead state definition.

Number of particles on dissociation

Model A treats water as an aqueous solution of ions (including chloride, sodium, sulphate, calcium, bicarbonate,

potassium and magnesium), these ions account for 99% of all the dissolved salts in seawater [9]. In Model A, the dead state is defined as pure water at ambient temperature (T_0) and atmospheric pressure (P_0) . As a consequence of this salinity dead state definition, the maximum specific concentration exergy occurs at maximum concentration levels and specific concentration exergy is a minimum in the purest water state.

Model B treats water as an ideal mixture of sodium chloride and water; the dead state is defined as the salinity of the incoming water at ambient temperature and atmospheric pressure. Therefore, the specific concentration exergy calculated using this model is at a minimum before purification. How does one select the most appropriate model, and do these two models give similar exergy analysis results? To investigate these questions, an initial model comparison was undertaken using a dataset from the literature [9].

Model A, which has been applied by several researchers, treats the systems under consideration as an aqueous solution of various ions. Mathematically, the general exergy equation (Eq. 1) is calculated using Eq. 2 when the intensive system measurements consist of temperature, pressure and concentration. Eq. 2 can be further broken down into the sum of three terms; a temperature exergy term, a pressure exergy term, and a concentration exergy term, Eq. 3 to Eq. 5.

$$Ex = \dot{m}(h - h_0 - T_0(s - s_0)) \tag{1}$$

$$Ex = \dot{m} \left[c_p (T - T_0) - c_p T_0 \ln \left(\frac{T}{T_0} \right) + \frac{P - P_0}{\rho} - N_{sol} R T_0 \ln x_{sol} \right]$$
 (2)

Where the thermal exergy term, Ex^{T} , is given by,

$$Ex^{T} = \dot{m} \left[c_{p} (T - T_{0}) - c_{p} T_{0} \ln \left(\frac{T}{T_{0}} \right) \right]$$

$$(3)$$

The pressure exergy term, Ex^{P} , is given by,

$$Ex^{P} = \dot{m} \left(\frac{P - P_0}{\rho} \right) \tag{4}$$

And the concentration exergy term, Ex^c , is given by,

$$Ex^{c} = -\dot{m}(N_{sol}RT_0 \ln x_{sol}) \tag{5}$$

$$N_{sol} = \frac{\left(1000 - \sum_{i} \frac{c_{i}}{\rho}\right)}{MW_{sol}} \tag{6}$$

$$X_{sol} = \frac{N_{sol}}{\left[N_{sol} + \sum \left(\frac{\beta_i c_i}{\rho M W_i}\right)\right]}$$
(7)

The symbols used are listed in the nomenclature section. Although the paper from which the dataset was obtained [9], does not explicitly state how the concentration values were obtained, a breakdown of seawater ionic composition and NF and RO rejection rates are given, as are MF and NF recovery rates. Following communication with the paper's corresponding author, the RO recovery rate was obtained (40.1%). From these values, the concentrations at various process stages can be calculated. The specific heat capacity value was not required in the exergy calculations due to the isothermal process stages. However, the density values at the various process stages were required to calculate the pressure and concentration exergy terms. Again, following correspondence with the corresponding author, the methodology used to calculate the density values was discussed. Model A has been used in various analyses; however, there is a slight discrepancy in the literature between the formulae used by some of the researchers. In some work [11, 20] the thermal exergy term, Ex^{T} , is defined as Eq. 1, which is considered the general exergy equation in other work by the same research group, in this other work, the thermal exergy term (Eq. 3) is used [9, 12, 13, 24]; perhaps this is only a typographical error but this remains unverified at the time of

Model B forms the basis of the exergy research carried out by several authors [15-17, 19, 25-29]. In Model B, the feedwater is treated as an ideal mixture of NaCl (salt) and pure water, where the salt mass fraction is based on salinity mass fraction. The total exergy of an ideal mixture can be found by calculating the enthalpy and entropy of the ideal mixture components and multiplying them by their respective mass fractions. One key assumption of Model B is that the different mixture constituents do not interact at the molecular level, therefore the enthalpy of mixing is zero. The entropy of mixing of an ideal mixture is not zero however, due to the fact that mixing is an irreversible process, and therefore the entropy of the ideal mixture, at a certain temperature and pressure, is greater than the sum of the entropies of the mixture components if they existed alone at the same temperature and pressure. The exergy for each process stage using Model B is calculated using Eq. 8. See references [15, 16] for complete derivation.

$$Ex = \dot{m} \begin{bmatrix} \left[(mf_{s}h_{s}) + (mf_{w}h_{w}) \right]_{Stage} - \left[(mf_{s}h_{s}) + (mf_{w}h_{w}) \right]_{DS} \\ -T_{0} \begin{bmatrix} mf_{s}s_{s}(T, P) + mf_{w}s_{w}(T, P) - \\ R_{im}(x_{s} \ln x_{s} + x_{w} \ln x_{w}) \end{bmatrix}_{Stage} \\ - \begin{bmatrix} mf_{s}s_{s}(T, P) + mf_{w}s_{w}(T, P) - \\ R_{im}(x_{s} \ln x_{s} + x_{w} \ln x_{w}) \end{bmatrix}_{DS} \end{bmatrix}$$
(8)

MODEL COMPARISON

Model A and Model B were compared using a dataset in the literature [9], the published information included ionic seawater composition, NF and RO rejection rates, temperatures, and pressures. The process stages, shown in Figure 1, included various pumps, MF, NF, two throttling valves (TV) and RO.

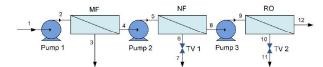


Figure 1 Desalination process stages from dataset, adapted[9]

To facilitate model comparison, the total dissolved solids (TDS) or concentration values of Model A (cited in Table 6 of reference [9]) were used as the basis for the salinity values for Model B. Salinity is defined differently to concentration, the concept of salinity was originally devised "as a measure of the mass of dissolved salts in a given mass of seawater [30]", or the mass fraction of sea salts. Generally in the literature, regarding Model B, salinity is equated to a mass fraction of NaCl. However, in order to use the concentration data in the cited dataset for the Model B analysis, the concentration values (mg/l) must be converted to mass fractions. To convert from mg/l to mass fraction requires the density Equating the mass fraction (ppm) and concentration (mg/l) is common for dilute aqueous solutions, but doing so assumes that the density of the aqueous solution is equivalent to the density of water at 4°C (1000kg/m³). However, seawater at 20°C and a typical salinity mass fraction of 3.5% has a density of approximately 1025kg/m³, according to the UNESCO International Equation of State of Seawater [31], which is a function of salinity, temperature and depth (or equivalent pressure).

As the process water gets more concentrated, for example, the retenate streams of the NF and RO processes, the density increases. As a consequence of increasing density, the direct conversion between mg/l and ppm becomes increasingly less accurate. Calculating an accurate density value for each stream is cumbersome. As a possible approximation, the International Equation of State of Seawater can be used to estimate density based on the dead state temperature and the relevant salinity. Salinity can be calculated as a function of the amount of chloride in the seawater [30]. However, due to the targeted ionic rejection of the NF and RO processes, the retenate and permeate streams are strictly no longer seawater. Therefore, calculating the salinity based solely on the chloride content is not feasible, one option is to use the total salts concentration rather than the more correct salinity input. In the authors' opinion, this is a reasonable approximation based on the previously quoted original purpose of the salinity concept. However, again, there is another issue which must be considered; calculating the density using the International Equation of State for Seawater requires an input of total salts (or salinity) as a mass fraction not mg/l, but conversion from mg/l to mass fraction requires the density. To overcome this issue, the density was approximated as follows;

- Equate concentration (mg/l) and mass fraction, use this value as an input to the International Equation of State for Seawater and calculate density
- Use the density value obtained to convert mg/l to mass fraction
- 3. Use the mass fraction of the total salts as the salinity value for Model B this is then equated to the NaCl mass fraction (as per the literature).

The concentration values obtained from the cited paper [9], were converted from mg/l to a mass fraction, the results are shown in Table 1. The second column in Table 1 shows the concentration values in mg/l, the third column contains the estimated density values obtained using the International Equation of State of Seawater, the final column shows the % difference in 'effective salinity' as a result of mg/l to ppm conversion. As expected, the process retenate streams (stages 6 and 10 in Figure 1) exhibit the largest % differences due to the estimated density increases.

Table 1 Concentration (mg/l) conversion to mass fraction

Stage	Conc. (mg/l)	Estimated Density (kg/m³)	Salinity (ppm)	% Difference mg/l - mf
1	34654	1024.5	33825.3	2.4
6	61852	1045.4	59165.9	4.3
8	25733	1017.7	25285.4	1.7
10	82567	1061.6	77776.0	5.8
12	270	998.4	270.4	-0.2

Although estimates, use of the relevant density value should give a better ppm estimate than solely equating mg/l with mass fractions. It should be stated that the International Equation of State for Seawater is only strictly valid for salinities between 0 and 42, therefore the densities calculated are estimates, intuitively though, the more concentrated the solution the greater the density.

The concentration, pressure and temperature values in the cited paper were used to develop a series of MATLAB programs to calculate the exergy rates using Model B. The X-Steam function was used to calculate the enthalpies and entropies of pure water at the various process stages. This function is available for free download at the MATLAB Central website [32]. Model B validation was carried out by comparing the exergy calculations obtained using Model B for an alternative exergy analysis dataset [15], with the calculations reported in the literature for that dataset, there was negligible difference. The exergy rates obtained in the cited paper [9] were compared to the exergy rates calculated using Model B.

MODEL COMPARISON RESULTS

The exergy rates calculated at each process stage using Models A and B are shown in Table 2; it is evident that the exergy rates calculated by both models are very different, this is expected due to the different salinity dead state definitions and the resulting differences in concentration exergy. The negative exergy rate values in the last column of Table 2 have been explained in the literature in different ways, (1) as a measure of the work input required to bring the retenate salinities back to the original dead state salinity [15], and (2) as the "potential use of rejected chemical exergy with respect to seawater. Commonly, this potential use is wasted in desalination facilities where rejected brine is merely returned to the sea. Then this loss of exergy represents the impact of waste on the surroundings [18]."

However, where the models should not differ significantly is in the exergy change or exergy destruction in each of the process stages. The change in exergy was calculated for each process stage; the change in exergy (or the exergy destruction) ΔEx is defined as the total 'exergy out' of each process minus the total 'exergy into' each process. A negative ΔEx value signifies that exergy has been destroyed and a positive value signifies that exergy has been added to the system (for example, via the three pumps). The ΔEx comparisons are shown in Table 3, it is clear that there are some considerable differences between the ΔEx values calculated by Model A and Model B. For ΔEx due to the three pumps, the % difference is not large and varies between 2.5 and 3.2%. However, it is the two important separation processes that yield the significant differences, namely the NF and the RO processes, 23.6% and 29.8% respectively. The difference in ΔEx between the models regarding the throttling valves, 6.1% and 7.7% respectively, is most likely a direct result of the preceding NF and RO separation processes.

 $\begin{tabular}{ll} \textbf{Table 2} & \textbf{Calculated Exergy rates comparison - Model A and Model B} \\ \end{tabular}$

Stage	Model A Exergy (KJ/hr)	Model B Exergy (KJ/hr)
1	2808300	0
2	2913300	101625
3	148800	0
4	2659500	0
5	3654500	962822
6	1334700	-858894
7	1113400	-1066672
8	1541300	1226921
9	6638300	6199037
10	3048909	-238405
11	1502074	-1666071
12	11327	3926046

Table 3 ΔEx comparison - Model A and Model B

Grouped Stage	Process	Model A ΔEx (KJ/hr)	Model B ΔEx (KJ/hr)	% D ifference ∆Ex
1	Pump 1	105000	101625	3.2
	MF	-105000	-101625	3.2
2	Pump 2	995000	962822	3.2
	NF	-778500	-594795	23.6
	TV 1	-221300	-207778	6.1
3	Pump 3	5097000	4972116	2.5
	RO	-3578064	-2511396	29.8
	TV 2	-1546835	-1427666	7.7

DEAD STATE DEFINITION

Why do these models differ? There are three main possibilities that can be investigated, including the dead state definition, the water constituency model and the exergy model calculation equations. In this paper, the focus is on the choice of dead state definition.

The influence of the dead state salinity was tested by amending the dead state definition in the series of MATLAB programs; the dead state was re-defined as pure water at ambient temperature and pressure (the same as Model A), and the MATLAB programs were rewritten accordingly. The results of this investigation are shown in Table 4 and Table 5.

Table 4 Calculated exergy rates comparison – Model B (original and amended Dead State) and Model A

Stage	Model B Original DS (KJ/hr)	Model B Amended DS (KJ/hr)	Model A (KJ/hr)
1	0	-8111370	2808300
2	101625	-8009744	2913300
3	0	-424881	148800
4	0	-7686488	2659500
5	962822	-6723666	3654500
6	-858894	-2751547	1334700
7	-1066672	-2959324	1113400
8	1226921	-4566914	1541300
9	6199037	405202	6638300
10	-238405	-2022906	3048909
11	-1666071	-3450572	1502074
12	3926046	-60112	11327

The calculated exergy rates for Model B, using both the original salinity dead state definition (incoming seawater) and the amended salinity dead state definition (pure water) are shown in Table 4, which also shows the exergy rates calculated using Model A. Originally, it was thought, that the main reason that the exergy rates calculated using Model A and Model B were significantly different was a result of the different salinity dead states; Table 4 shows that this is not the case. In fact, when the salinity dead state was amended to pure water, all the previously positive Model B exergy rates (Table 2, column 3) changed to negative values, except State 9 (large pressure exergy input due to high pressure pump). Mathematically, due to the amended dead state Eq. 8 simplifies to Eq. 8a, shown below.

$$Ex = \dot{m} \begin{bmatrix} [(mf_{s}h_{s}) + (mf_{w}h_{w})]_{Stage} - [(h_{w})]_{DS} \\ -T_{0} \begin{bmatrix} [mf_{s}S_{s}(T, P) + mf_{w}S_{w}(T, P) -] \\ R_{im}(x_{s} \ln x_{s} + x_{w} \ln x_{w}) \end{bmatrix}_{Stage} \\ -[S_{w}]_{DS} \end{bmatrix}$$
(8a)

There are two causes of the negative exergy rates that come about as a result of the amended salinity dead state, one cause relates to changes in enthalpy and the other to changes in entropy;

1. At the majority of process stages, $h-h_0<0$, this occurs because the enthalpy of water in the pure state is now greater than the enthalpy of the ideal mixture, see Eq. 8 and Eq. 8a. The lower enthalpy of the ideal mixture is due to the presence of the salt (i.e. the heat capacity of salt in the ideal mixture lowers the overall enthalpy of the ideal mixture). There are two exceptions, process stages 9 and

- 10, where the high pumping pressure input counteracts the negative value of enthalpy differences. Process stage 10 is still at relatively high pressure, the pressure drop tangential to the RO membrane is 1 bar (from 69 bar at process stage 9 to 68 bar at process stage 10).
- 2. At all process stages, $s-s_0>0$. Therefore, when multiplied by $(-T_0)$, the product is always negative. In the original dead state salinity definition, $s-s_0<0$ except for cases where the salinity at the relevant process stage was greater than the dead state salinity (NF, RO, and their respective throttling valves), these exceptions contributed to negative exergy rates in the original dead state definition.

Table 5, column 3 shows the absolute % difference of exergy change calculated by the models (previously shown in the last column of Table 3). The last column of Table 5 shows the absolute % difference of exergy change, but this time using the amended dead state definition. These results indicate that the dead state definition has very little impact on the exergy change calculations with respect to the original model dead state definition; however, there is a slight change in the RO process, a 0.7% increase. In the authors' opinion, this increase is relatively insignificant when compared to the magnitude of the exergy change calculation differences between the two models. Therefore, the salinity dead state definition does not have a significant impact on the ΔEx values calculated by the two models, however, it does have an impact on the exergy rates calculated using the Model B MATLAB programs.

Table 5 ΔEx comparison – % Difference in ΔEx calculated by Model A and Model B (original and amended Dead States)

Grouped Stage	Process	%Difference ΔEx (Original DS) (KJ/hr)	%Difference ∆Ex (Amended DS) (KJ/hr)
_2(Pump 1	3.2	3.2
1	MF	3.2	3.2
_	Pump 2	3.2	3.2
2	NF	23.6	23.6
	TV 1	6.1	6.1
	Pump 3	2.5	2.5
3	RO	29.8	30.5
	TV 2	7.7	7.7

CONCLUSION

This paper carried out an initial comparison of two prevalent desalination exergy models, Model A and Model B, using a dataset from the literature. In order to compare the two models, concentrations in mg/l were converted to ppm using estimated density values based on the International Equation of State of Seawater. A series of MATLAB programs was then written to calculate the exergy values at the various process stages based on process information from the dataset. Both the exergy rates and the change in exergy/exergy destruction (ΔEx)

values calculated with Model A and Model B were compared. The calculated exergy rates were very different, this was somewhat expected due to the different dead state definitions. However, ΔEx values calculated with each model also showed significant differences, a 29.8% and a 23.6% difference for the RO and NF processes respectively.

An initial investigation into the salinity dead state influence was undertaken; the salinity dead state definition of Model B was changed to that of Model A. This resulted in negligible difference in the exergy destruction rates calculated. However, the amended dead state definition did result in significant changes in the exergy rates calculated by both versions of Model B.

In summary, based on information obtained from a dataset in the literature, and assuming that the exergy rates were accurately calculated;

- The exergy rates calculated using Model A and Model B differed significantly, exergy rates calculated using Model A are positive, exergy rates calculated using Model B can be positive or negative (depending on the stream concentration with respect to the salinity dead state).
- Although more aligned than the exergy rates, there are significant differences between the exergy destruction rates calculated for the NF and RO processes using Model A and Model B.
- The amended dead state does not affect the exergy destruction rates calculated with Model B, however, it does have an important influence on the exergy rates calculated at each process stage.

Considering that the principal purpose of an exergy analysis is to identify system irreversibilities and to focus improvement efforts, this 29.8% deviation in RO exergy destruction between the two models is worrying. Based on this work, it would suggest that either, one of the models is reasonably accurate and the other model is significantly over- or under-estimating the exergy destruction in the key separation processes or neither model is sufficiently accurate. Further research is required to investigate these model discrepancies and to determine which of these models is the most suitable and accurate for calculating desalination exergy rates, or perhaps to develop a different, more accurate desalination exergy model.

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