



## Exergy analysis of water purification and desalination: A study of exergy model approaches



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### HIGHLIGHTS

- Several desalination exergy model approaches are examined, both theoretically and practically.
- The assumptions and limitations of these models are assessed.
- The models are compared using a desalination plant dataset.
- Significant differences were found in the results of the exergy analyses obtained.
- Certain models may not be suitable for desalination plant exergy analyses.

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### ABSTRACT

In the literature, several exergy analysis approaches have been proposed to investigate desalination processes. It is not clear, however, which approach is the most appropriate or indeed whether all approaches are valid. The objective of this paper is to review the various methods and to critically assess their assumptions, limitations, advantages and disadvantages. The main focus of this work is the chemical exergy term. Several exergy calculation models were examined and compared using a dataset from the literature. In addition, an accurate approach to calculate the chemical exergy of electrolyte solutions, based on the Pitzer equations, was proposed. The models assessed were: (1) the ideal mixture model (NaCl and water), (2) the ideal mixture model (seawater salt and water), (3) the Sharqawy seawater functions, and (4) the electrolyte solution model (Pitzer equations, NaCl and water), (5) the model used by Drioli et al. and (6) the dissociated ion approach (NaCl and water). Four of the six approaches produced very similar results. Moreover, one other exergy calculation method was found to have serious limitations. The findings presented here show that the choice of exergy model can have a significant impact on the results obtained and that considerable care must be taken to select the most suitable approach.

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### 1. Introduction

Water and energy are inextricably linked; energy is required to treat water and water is required to source and convert primary energy. The water–energy nexus is receiving due consideration as pressures on both energy and water resources increase. According to Olsson [1], water and energy systems and operations should be planned together. The close association is very true of water treatment processes, which are becoming increasingly necessary to meet various water demands including potable, industrial and agricultural water requirements. Water purification technologies are manifold, for example, multi-stage flash distillation (MSF), multi-effect distillation (MED) and reverse osmosis (RO), and the application of these technologies ranges from large seawater

desalination processes to ultra-pure water (UPW) applications in the pharmaceutical, semiconductor or power generation industries. The energy requirements vary significantly between applications, and from process to process. For example, high-end applications such as UPW have a greater energy footprint than potable water treatment, and, in general, thermal processes such as distillation are more energy intensive than membrane processes such as reverse osmosis or nanofiltration (NF). Table 1 collates data from several sources in the literature and illustrates the specific operating energy requirements for various purification processes. It is evident that the MSF and MED technologies consume significantly more specific energy than the seawater reverse osmosis process. According to Table 1, however, there is also a large deviation between the highest and lowest values of specific energy for the MSF and MED processes, which may signify potential scope for improvement. The energy requirements for high purity applications such as semiconductor UPW vary between 9.55 and 10.24 kWh/m<sup>3</sup> respectively [2,3].

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**Table 1**  
A comparison of water purification process specific operating energy requirements.

Water purification technology	Energy (kWh/m <sup>3</sup> )	Reference
Brackish water RO (core process)	1	[4]
Seawater RO with energy recovery (core process)	2.2 to 2.7	[4,5]
Seawater RO (all auxiliary requirements)	5 to 7	[5,6]
MSF	16 to 20	[7,8]
MSF (all auxiliary requirements)	38.5 to 125	[6]
MED	14	[8]
MED (all auxiliary requirements)	32 to 122.5	[4]
Ultra-pure water RO (all auxiliary requirements)	9.55 to 10.24	[2,3]

Energy research in desalination processes is well-established and has contributed to lowering the water treatment energy footprint. In relation to RO processes, the energy footprint had dropped from approximately 20 kWh/m<sup>3</sup> in the 1970s to a value of less than 2 kWh/m<sup>3</sup> by 2004 [9]. According to reports, a more recent value of 1.58 kWh/m<sup>3</sup> has been achieved under ideal conditions (new membrane, low water flux at 42% recovery) [10]. It should be stated, however, that this low specific energy value was obtained at the expense of permeate quality. Several factors have contributed to these significant achievements including improved membranes [9,11]; pump and motor efficiency improvements [9,12] and the use of variable speed drives (VSD); studies in RO system optimisation [13–18]; and the implementation of energy recovery devices such as pressure exchangers, and Pelton and Francis turbines to harness wasted throttling valve energy [19,20].

One approach that has been widely accepted as a useful analytical tool for the characterisation and optimisation of water purification and desalination systems is exergy analysis. However, researchers in this area have used a variety of exergy model approaches to determine the exergy of aqueous solutions such as seawater and brackish water. Primarily, the various approaches differ in three ways:

1. The dead state definition
2. The modelling of the aqueous solution
3. The exergy calculation equation.

Regarding the dead state definition, the majority of researchers define the dead state as the ambient temperature, pressure and salinity of the seawater/brackish water in question. In contrast, other research groups have defined the dead state as that of pure water [5,21,22]. The impact of dead state selection has been investigated by several researchers [23,24]. In relation to the thermodynamic chemical exergy model of seawater and other relevant aqueous solutions, various assumptions have included both ideal behaviour [25–29] and non-ideal mixture behaviour [30–33], and even pure water [34]. Where ideal mixture behaviour has not been assumed, activity coefficient calculation models such as the Debye–Hückel limiting equation have been proposed and used [33,35,36]. Finally, the equations used to calculate the exergy rates differ significantly between research groups. The majority of researchers [5,26,30,31,33,35,37,38] split the exergy rate calculation of aqueous solutions into physical and chemical exergy terms, whereas others [25,39] couple the physical and chemical exergy rates implicitly. In addition, some researchers have used thermodynamic properties of seawater [38,40] to calculate the exergy rates.

To date, limited comparisons between the various approaches have been presented in the literature. Sharqawy et al. [38] found differences of up to 80% between the exergetic efficiency values calculated for a seawater MSF desalination plant using updated thermodynamic properties of seawater in comparison with the exergy calculation model proposed by Cerci et al. [25,39]. Other researchers compared the Cerci and Drioli approaches and found differences of up to 30% between the exergy destruction rates calculated. In that case, the major differences between the two approaches occurred in the key separation technologies, indicating that the source of the difference was the calculation of chemical exergy [24]. Sharqawy [38] showed mathematically that the flow exergy of a binary ideal mixture was always positive; however,

Kahraman et al. [25], while purporting to use an ideal mixture model, reported negative values of flow exergy. Furthermore, as noted by many authors, seawater and other electrolyte solutions are not ideal mixtures. It is evident that it is not a trivial exercise to tease out the different approaches.

With this in mind, the objectives of this work are: (1) to examine and assess the current exergy calculation models for desalination exergy analyses; (2) to propose a general approach applicable to electrolyte solutions, including an assessment of activity calculation methods; and (3) to compare and assess the impact of the various approaches on the exergy analysis of a desalination plant using a dataset from the literature.

## 2. Exergy analyses of desalination/water purification plants

Exergy analysis considers energy in terms of both quantity (First Law of Thermodynamics) and quality (Second Law of Thermodynamics). Generally, in desalination analyses, the thermodynamic property exergy is broken down into physical and chemical exergy contributions. One key exception is the approach proposed by Cerci [39,41], where the physical exergy and chemical exergy are integrated, i.e. the chemical/concentration exergy is implicitly included in the entropy of mixing differences. Velocity and elevation contributions are included if applicable, but this is not generally the case for desalination plants. Practically, water purification technologies such as MSF or RO plants are typically modelled as a series of processes, where each process is modelled as a control volume in steady state. The exergy rates are calculated at the relevant process stages and then an exergy balance is used to determine: (1) the exergy rates, the exergy destruction rates and the key sites of exergy destruction; and (2) the exergetic efficiency of individual process components and the overall process. The exergy balance identifies and quantifies the main sources of thermodynamic irreversibilities in the sequence of processes. However, unlike entropy balances, which are a function of the system alone, exergy balances are a function of both the system and the defined dead state. Therefore, the choice of dead state is important to gain insight into the availability at each process stage; this is particularly important in the assessment of waste streams which are rejected to, and mix with, the environment.

Many researchers have applied exergy analyses to characterise desalination/water purification processes, and several exergy models have been utilised, see Table 2. Of the models presented, the first is based on the specific thermodynamic properties of seawater; others are based on more general modelling approaches that model seawater or other aqueous solutions as a combination of pure water and salts. Until recently, however, exergy analyses have been carried out in relative isolation. The various models in Table 2 have been applied by different research groups, but the results obtained using these models have not been assessed comprehensively, or more importantly, the limitations or validity of these models has not been examined. The choice of exergy models proposed in the literature poses a significant challenge to potential exergy researchers: do these models give similar results? Or, if not, which is the most appropriate exergy model to use for desalination/water purification purposes?

The electrolyte solution model presented in Table 2 has been previously used in the literature for both aqueous solutions and desalination exergy analyses [31,33,35]. However, according to Spiegler and El-Sayed, the use of the electrolyte solution model is problematic because “most of the activities of salt species are either unknown, uncertain or difficult to evaluate [31]”. Consequently, not only does this research assess and compare the various modelling approaches, but it also evaluates the important considerations associated with modelling electrolyte solutions.

## 3. Desalination/water purification exergy models

When a system is in physical and chemical equilibrium with the dead state the opportunity to do work no longer exists and the exergy

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