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Energy savings in desalination technologies: reducing entropy generation by transport processes

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Desalination systems can be conceptualized as power cycles in which the useful work output is the work of separation of fresh water from saline water. In this framing, thermodynamic analysis provides powerful tools for raising energy efficiency. This paper discusses the use of entropy generation minimization for a spectrum of desalination technologies, including those based on reverse osmosis, humidification-dehumidification, membrane distillation, electrodialysis, and forward osmosis. Heat and mass transfer are the primary causes of entropy production in these systems. The energy efficiency of desalination is shown to be maximized when entropy generation is minimized. Equipartitioning of entropy generation is considered and applied. The mechanisms of entropy generation are characterized, including the identification of major causes of irreversibility. Methods to limit discarded exergy are also identified. Prospects and technology development needs for further improvement are mentioned briefly.

Introduction
Desalination of seawater, brackish water, and wastewater has gained increasing importance in the face of rising population and changing climate [1]. As of June 2017, global desalination capacity exceeded 92 Mm³/day [2]. The energy efficiency of desalination plants has improved steadily over recent decades, but, for seawater desalination, energy still represents 30 to 40% of the cost of water. Today’s state-of-the-art seawater reverse osmosis plants require 3 to 4.5 kWh/m³ of the cost of water. Today’s state-of-the-art seawater reverse osmosis plants has improved steadily over recent decades, and changing climate [1]. As of June 2017, global desalination gained increasing importance in the face of rising population feed salinity, water recovery ratio, and plant characteristics.

Figure 1 Control volume for a desalination plant

source can also effect the separation, as in a variety of distillation processes. The First and Second Laws of Thermodynamics may be applied to a control volume surrounding the desalination system in steady state:

\[ W_{sep} + \dot{Q} + (\dot{m}h)_{sw} = (\dot{m}h)_p + (\dot{m}h)_b \]  

(1)

\[ \frac{\dot{Q}}{T_0} + (\dot{m}s)_{sw} + S_{gen} = (\dot{m}s)_p + (\dot{m}s)_b \]  

(2)

In Eqs. (1) and (2), \( T_0 \) is the ambient temperature of the environment away from the system (to which heat is rejected), \( \dot{m}_i, h_i, \) and \( s_i \) are the mass flow rate, specific enthalpy and specific entropy of the saline water (sw), product (p), and brine (b) streams [3]. Heat and work are considered to be positive if they enter the system. Elimination of \( \dot{Q} \) between these equations gives the work of separation

\[ W_{sep} = \dot{m}_p(h-T_0s)_p + \dot{m}_b(h-T_0s)_b - \dot{m}_{sw}(h-T_0s)_{sw} + T_0S_{gen} \]  

(3)

In the case that that the entering and leaving streams are at the dead state pressure and temperature, \( T_0 \) and \( p_0 \),

\[ W_{sep} = \dot{m}_p g_p + \dot{m}_b g_b - \dot{m}_{sw} g_{sw} + T_0 S_{gen} \]  

(4)

where \( g = h - Ts \) is the specific Gibbs free energy.¹

¹All values are approximate and depend on various local considerations, including feed salinity, water recovery ratio, and plant characteristics.

²An identical result is obtained if a control mass is considered rather than a control volume [6, footnote 7], although obviously without the dots above the symbols.

Desalination as a thermal power cycle

The basic operation of a desalination process is to separate a saline feed stream into a more pure product stream and a more saline brine stream (Fig. 1). Work is required to effect this separation, as provided, for example, by pumps in reverse osmosis desalination. Equivalently, heat transfer from a higher temperature

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The least work occurs for a reversible desalination plant, with \( \dot{S}_{\text{gen}} = 0 \):
\[
W_{\text{least}} = \dot{m}_p E_p + \dot{m}_b E_b - \dot{m}_{sw} E_{sw}.
\]
(5)

The least work is independent of the desalination process and depends only on the differences of Gibbs energy between the entering and leaving streams. For saline water, this means that the least work will depend on the feed salinity, the pure water recovery ratio \( r = \dot{m}_p/\dot{m}_{sw} \), and, if the product is not essentially pure, the product water salinity. Least work is shown as a function of recovery ratio in Fig. 2 using the ionic composition of seawater at various concentrations (saline water properties are discussed in Appendix A). The minimum value of the least work, \( W_{\text{least}}^{\text{min}} \), occurs for infinitesimal recovery ratio \( r \rightarrow 0 \) as if extracting just a small cup of pure water from an ocean of salty water.

If the leaving streams are at a temperature different from the dead state, exergy is being discarded as the streams exit, meaning that the work requirement will be greater than if the streams are at the dead state temperature. Streams leaving at pressures above the dead state pressure is negative [7]. In addition, when the leaving streams are at the dead state temperature, the reversible system produces leaving streams of lower total entropy than the entering stream, so that heat must be rejected to the environment, according to Eq. (2). If the system operates adiabatically (\( Q = 0 \)), the leaving streams have higher enthalpy (are warmer) than the entering stream, and the higher outlet temperature strongly raises the outlet entropy for a given level of separation. Consequently, entropy usually must be generated, and the work requirement will be greater than if the streams exit at the dead state temperature.

**Exergetic formulation.** In the case that the outlet conditions are not at the dead state temperature and pressure, Eq. (3) may be recast in terms of the flow exergy function [6, 7]:
\[
e_f = (h - h^*) - T_0 (s - s^*) + \sum_{k=1}^{n} \dot{w}_k \left( \mu_k^* - \mu_{k,0} \right) / M_k
\]
(6)

where a superscript * denotes that the temperature and pressure, but not the concentration, are at the environment condition (the restricted dead state); and subscript 0 denotes that temperature, pressure, and concentration are at the environment condition (the global dead state). Streams leaving a desalination plant are by design not at the environment’s concentration. The result, using the fact that \( \dot{m}_{sw} = \dot{m}_b + \dot{m}_p \), is
\[
W_{\text{sep}} = \dot{m}_p e_f + \dot{m}_b e_f - \dot{m}_{sw} e_{sw} + T_0 \dot{S}_{\text{gen}}
\]
(7)

where the last term represents exergy destruction. In the case that the leaving streams are at the restricted dead state, Eq. (7) reduces to Eq. (4).

**Distillation.** If a desalination system operates by taking in a high temperature heat input, \( \dot{Q}_{\text{sep}} \) at \( T_H \), as opposed to a work input, \( W_{\text{sep}} \), then some algebra shows that the work term in either Eq. (4) or (7) may be replaced by the exergically equivalent amount of heat:
\[
\dot{Q}_{\text{sep}} \left( 1 - \frac{T_0}{T_H} \right) = W_{\text{sep}}
\]
(8)

As before, the plant may still reject heat to \( T_0 \). Most distillation plants require both a heat and a work input (the latter being for liquid circulation pumps), so that a sum is needed on the lefthand side of the two equations mentioned, e.g.,
\[
\dot{Q}_{\text{sep}} \left( 1 - \frac{T_0}{T_H} \right) + \dot{W}_{\text{pump}} = \dot{m}_p e_f + \dot{m}_b e_f + \dot{m}_{sw} e_{sw} + T_0 \dot{S}_{\text{gen}}
\]
(9)

**Second-law efficiency.** The second-law efficiency of a desalination plant, with respect to the exergy input that it receives, is [5, 6, 8, 9]
\[
\eta_H = \frac{\text{least exergy of separation}}{\text{exergy input to plant}}
\]
(10)

where \( W_{\text{sep}} \) or \( \dot{Q}_{\text{sep}} \) and \( \dot{W}_{\text{pump}} \) may be zero depending upon the system in question. Equations (7) and (9) show that \( \eta_H \) is maximized by minimizing the entropy generation and bringing the outlet streams toward the restricted dead state.

The second-law efficiency of a number of desalination plants at various feedsalinities has been reported by Tow et al. [10]. Typical large seawater RO plants have a second-law efficiency in the range of 25 to 35%. For cases of combined water and power production, the second-law efficiency may instead be referred to primary energy [6, 8]. Altmann et al. [11] have assessed primary energy efficiency for a wide variety of desalination plants. Second-law analysis has also been applied to zero-liquid discharge desalination systems [12, 13].

**Entropy generation by transport processes**

Carrington and Sun [14] and Kjelstrup et al. [15] have shown that the entropy generation per unit volume, \( \sigma \), is given by
\[
\sigma = \nabla \cdot J_U + \sum_k \left[ \frac{\dot{z}_k \vec{E} \cdot \vec{J}_k}{T} - \nabla \left( \frac{\mu_k}{T} \right) \right] \cdot \vec{J}_k
\]
(12)

where \( \dot{z}_k \) is the chemical potential per mole of species \( k \), \( \vec{J}_k \) is the molar flux of \( k \), \( \vec{E} \) is the electric field vector, \( F \) is Faraday’s number, and \( \dot{z}_k \) is the valence of \( k \). Equation (12) accounts for entropy generation by heat and mass diffusion and by electric current. The internal energy flux \( J_U \) is related to the measurable heat flux \( J_Q \) by
\[
J_U = J_Q + \sum_k \dot{h}_k \vec{J}_k
\]
(13)

where \( \dot{h}_k \) is the molar enthalpy of species \( k \). The electric current density \( \vec{J} \) is
\[
\dot{J} = F \sum_k \dot{z}_k \vec{J}_k
\]
(14)
With \( \mu_k = \tilde{h}_k - T \tilde{s}_k \), for \( \tilde{s}_k \) the molar entropy of species \( k \),

\[
\sigma = \frac{1}{T} \cdot \mathbf{J}_Q + \frac{1}{T} E \cdot \mathbf{j} + \frac{1}{T} \left( \sum_k \tilde{h}_k \mathbf{J}_k \right) - \sum_k \left( \frac{\mu_k}{T} \right) \cdot \mathbf{J}_k 
\]

(15)

\[
= \frac{1}{T} \cdot \mathbf{J}_Q + \frac{1}{T} E \cdot \mathbf{j} - \frac{1}{T} \sum_k (\nabla \tilde{h}_k - T \nabla \tilde{s}_k) \cdot \mathbf{J}_k 
\]

(16)

The last two terms in Eq. (16) are essentially the gradient of chemical potential evaluated at a constant temperature (i.e., by considering only its dependence on concentration and pressure), a point that has occasionally been overlooked. This gradient may be compactly denoted as \( \nabla_T \):

\[
\sigma = \frac{1}{T} \cdot \mathbf{J}_Q + \frac{1}{T} E \cdot \mathbf{j} - \frac{1}{T} \sum_k \nabla_T \mu_k \cdot \mathbf{J}_k 
\]

(17)

Terms accounting for viscous dissipation term and chemical reactions may be added to the entropy production if it is relevant to do so. For further discussion, see the lucid development in Kjelstrup et al. [15, Chap. 3, App. A].

**Entropy generation minimization and equipartitioning**

Equations (4), (7), and (9) show that the energy consumption of a desalination plant may be minimized by: i) minimizing entropy generation with respect to fixed conditions of water production, \( m_p \), and water recovery ratio, \( r \); and ii) bringing the outlet stream temperature and pressure closer to the restricted state, and so as to avoid discarding useable exergy. In view of the second consideration, pressure recovery devices (e.g., turbines or pressure exchangers) are essential components in reverse osmosis plants that produce an appreciable amount of high-pressure brine; and heat recuperation is essential the design of all distillation plants [17].

The first consideration leads to a need to minimize differences (or gradients) in temperature, concentration, or pressure throughout the system. Some straightforward ideas can be drawn from heat exchangers. Counterflow designs can transfer a given amount of heat between streams at different inlet temperatures while maintaining low local temperature differences. Further, balancing the heat capacity rates of the two streams [setting \( (mc_p)_h = (mc_p)_c \)] can make the local temperature difference between streams, \( \Delta T \), uniform over the length of the counterflow exchanger (Fig. 3). A balanced, counterflow heat exchanger has the minimum entropy generation for a given pair of inlet temperatures and heat exchanger effectiveness [18]. The concept of balanced counterflow has been extended to several desalination technologies, such as reverse osmosis, humidification-dehumidification, membrane distillation, and forward osmosis; and it has long been embedded in multistage flash and multi-effect desalination systems [17].

A balanced counterflow device having a given local \( \Delta T \) can transfer a fixed amount of heat using less area, \( A \), when the overall heat transfer coefficient, \( U \), is larger. Alternatively, a larger \( U \) can facilitate a lower \( \Delta T \) for a given area. Since the local entropy production of a small area \( dA = \mathcal{P} \cdot dx \) is

\[
dS'_{gen} = dQ \left( \frac{1}{T_c} - \frac{1}{T_h} \right) \approx \frac{dQ \Delta T}{T_c^2} = \frac{U \mathcal{P} \Delta T^2}{T_c^2} \cdot dx
\]

(18)

Thus, \( \sigma \) is quadratic in the driving forces, e.g., proportional to square of temperature or concentration gradients:

\[
\sigma = \sum_i X_i \cdot \mathbf{J}_i
\]

(20)

where the combinations can be seen by inspection. Further, for many systems, the fluxes are an isotropic linear function of the driving forces:

\[
\mathbf{J}_i = \sum_j L_{ji} X_j
\]

(21)

Thus, \( \sigma \) is quadratic in the driving forces, e.g., proportional to square of temperature or concentration gradients:

\[
\sigma = \sum_{i,j} X_{i} L_{ji} X_{j}
\]

(22)

Tondeur and Kvaalen [21] considered systems of this type with a constant coupling matrix \( L_{ij} \) and operated at a fixed duty (amount of heat or mass to be transferred). They proved that reducing the spatial variance of the driving force (or the summed covariance for multiple forces) will minimize the overall entropy generation, assuming that the forces can be independently varied [22]. Indeed, that is exactly what is accomplished by balancing a counterflow heat exchanger to produce a uniform \( \Delta T \) and minimize entropy.

\[\text{Equation 19}\]

The pairings in Eq. (17) are similar to, but not the same as, those in Eq. (12). The relationship of driving forces to a fundamental equation for entropy is discussed by Callen [19] and Bejan [20], and various pairings are given in [15].
Reverse osmosis

Reverse osmosis accounted for 65% of the world’s desalination capacity in 2015 [29]. RO is the dominant technology for brackish groundwater desalination and is rapidly displacing traditional thermal technologies for seawater desalination. The energy requirements for seawater RO were described in the introduction. For brackish water desalination, the pump pressures required are much lower (feeds have just 3 to 20% of seawater’s salinity); but cost optimization favors less energy-efficient systems that typically consume 0.3 to 1.5 kWh/m³ [30].

Various RO configurations are used depending on the condition of the saline feed water. We will focus on a basic single-stage seawater configuration (Fig. 4). Seawater enters at ambient pressure and is divided into two streams, one going directly to a high pressure pump and one entering a rotary pressure exchanger. Once both streams are brought to high pressure, they enter the RO membrane module. Low pressure fresh water and high pressure brine exit the module. The high pressure brine is sent to the pressure exchanger, which transfers enthalpy from the brine to the feed with high isentropic efficiency. The brine exits the system at ambient pressure. The pressure exchanger is essential in recovering brine energy after the RO module, bringing it close to the restricted dead state. Pressure recovery devices can lower energy consumption substantially and are universally applied in seawater systems, for which brine pressures are high and recovery ratios are limited.

In the RO module, the high pressure saline feed enters on one side of a semi-permeable membrane and flows along the membrane. Water passes through the membrane, leaving most salts behind. As water is removed, the feed salinity rises, causing the osmotic pressure to rise over the length of the module. A typical distribution of hydraulic and osmotic pressure in a seawater RO module is shown in Fig. 5. The inlet hydraulic pressure must be high enough that the outlet (or brine) hydraulic pressure exceeds the outlet osmotic pressure, so that water can be forced through the membrane. Consequently, significantly more pressure is applied near the inlet than is necessary to produce water flux. The excess pressure generates substantial entropy: Mistry et al. showed that more than 50% of a representative RO system’s entropy generation occurs as a result of the pressure difference across the membranes [3]. This effect can be shown as follows.

The chemical potential of water in a saline solution is given by

$$\mu_w = \bar{g}_w + RT \ln (a_{w_0})$$  \hspace{1cm} (23)

where $\bar{g}_w$ is the molar Gibbs energy of pure water, $a_{w_0}$ is the activity of water in solution, and $R$ is the universal gas constant. The effect of hydraulic pressure on Gibbs energy has essential importance. For the pure substance:

$$\frac{\partial \bar{g}_w}{\partial p} = \bar{v}_w$$  \hspace{1cm} (24)

where $\bar{v}_w$ is the molar volume of pure liquid water. The osmotic pressure of water in solution relative to pure water is

$$\Pi_w = -\frac{RT \ln (a_{w_0})}{\bar{v}_w}$$  \hspace{1cm} (25)

In this equation, the liquid is assumed to be incompressible so that the molar volume is independent of pressure.

To evaluate the entropy generation resulting from the transport of water through a membrane using Eq. (17), $\nabla_T \mu_w$ is required:

$$\nabla_T \mu_w = \nabla_T (\bar{g}_w + RT \ln (a_{w_0}))$$  \hspace{1cm} (26)

$$= \bar{v}_w \nabla_T p - \bar{v}_w \nabla_T \Pi_w$$  \hspace{1cm} (27)

$$= \bar{v}_w \nabla_T (p - \Pi_w)$$  \hspace{1cm} (28)

With this result, integration of $\sigma$ across the membrane thickness $L$ gives the entropy generation per unit membrane area:

$$S_{gen} = \int_0^L \sigma \, dx = \int_0^L \left[ \nabla_T \cdot \mathbf{J}_Q - J_w \bar{v}_w \frac{\nabla_T (p - \Pi_w)}{T} \right] \, dx$$  \hspace{1cm} (29)

$$= J_Q \left( \frac{1}{T_L} - \frac{1}{T_0} \right) + \bar{v}_w J_w \frac{\Delta p - \Delta \Pi_w}{T}$$  \hspace{1cm} (30)
where $\Delta$ means feed value minus permeate value. The membrane's salt rejection is approximated to be 100%. The first term is the usual entropy production by heat transfer through a temperature difference; and for entire RO pressure vessels the temperature rise tends to be quite small (≈0.5 K) [6] with unimportant heat fluxes, so this term is negligible. The water flux is expressed phenomenologically by the solution-diffusion model [31–33] as

$$J_w = A (\Delta p - \Delta \Pi_w)$$  \hspace{1cm} (31)

where $A$ is the membrane permeability in consistent units. Thus,

$$\varepsilon_{\text{gen}} = \frac{v_m A}{T} (\Delta p - \Delta \Pi_w)^2$$  \hspace{1cm} (32)

The overpressurization seen near the inlet in Fig. 5 thus contributes greatly to the entropy generation and energy inefficiency of RO desalination. The standard configuration (Fig. 5) is far from equipartitioning [26]. Various different designs have been developed to counteract this effect, leading to better equipartitioning, including the following.

1. **Multistage RO**, in which two or more sets of pumps and pressure vessels are placed in series, so that the first stage operates at a lower pressure, removing some of the water from the feed. Following stages use higher hydraulic pressures as the osmotic pressure becomes larger, recovering more water [35, 36]. Energy is saved because the hydraulic and osmotic pressures in the initial stage are closer than on the left side of Fig. 5. Multistage seawater plants have been demonstrated to save energy and achieve high water recovery ratios [36].

2. **Batch RO**, in which a batch of saline feed is pressurized gradually as water is removed and the osmotic pressure rises [34, 37, 38]. Figure 6 shows a simplified conceptual arrangement. Practical considerations may limit the energy savings for seawater operation in certain configurations, while brackish water operation has shown the potential for energy efficiency in these two heat and mass exchangers helps to limit the amount of exergy discarded with the leaving streams, also reducing $\dot{Q}$ [50]. The energy (first-law) efficiency of HDH is usually characterized the gained-output-ratio, or GOR:

$$\text{GOR} = \frac{h_{\text{fg}} m_p}{\dot{Q}}$$  \hspace{1cm} (33)

which compares the latent heat required to vaporize the product water to the heat input. Well-designed experimental systems have reported GOR values as high as 2.6 for a single-stage system and up to 4.0 for a two-stage system [51].

The entropy production in HDH results primarily from heat and mass transfer in the gas phase. Thiel et al. [24] showed that Eq.

![Figure 6 Batch RO system with high pressure, variable-volume tank [34]. The system is filled with feed, which is gradually pressurized and concentrated during a single cycle. Dotted flows (refill and brine reject) occur between cycles.](image)

![Figure 7 Schematic drawing of a basic open-air, closed-water HDH system.](image)
the entropy production of the entire system is dominated by the dehumidifier, with the result that system performance is controlled by the HCR of the dehumidifier, HCR_d (Fig. 8). Further, Chehayeb et al. [27] showed that entropy generation is minimized at the balanced condition, HCR_d = 1 (Fig. 9), as is the spatial variation of entropy production, indicating that the balanced condition is consistent with equipartitioning. Multistage designs allow further opportunities for balancing by extracting air from the humidifier to the dehumidifier at an appropriate intermediate point [27, 54–56]. Industrial systems often use one such extraction. Significant interest has surrounded the potential to drive HDH systems with solar energy [57–59], although such designs have not been operated at large scale. Plate dehumidifiers have been considered [60, 61], but research around direct-contact components, especially bubble columns, has been most promising and has gone on to industrial use [62–68]. In particular, shallow bubble columns (similar to low-profile air strippers) can minimize hydrostatic pressure losses and blow power demand.

Membrane distillation

Membrane distillation is an emerging technology that can operate on low-grade heat, such as solar thermal energy. A variety of designs have reached an early commercial stage, but deployment has quite limited. Pilot-scale seawater MD systems have reported GOR values up to 7 (90 kWh/m³) with electrical consumption of 0.13 kWh/m³ [69]. Research in this area is very active.

Membrane distillation is in many ways similar to HDH desalination, in that water is vaporized from a warm saline stream and condensed in a counterflow, heat recuperation arrangement [70–72]. However, in MD systems, the saline stream is separated from the cooler, pure stream by a hydrophobic, porous membrane through which vapor alone can pass. In direct-contact MD (Fig. 10), the warm saline feed flows counter to a cool pure water stream which is in a separate flow loop. Vapor leaves the feed, passing through pores in the hydrophobic membrane, and being condensed into the pure stream. In air-gap membrane distillation

\[ \Delta H_{\text{max}} = \frac{\Delta H_{\text{max, cold}}}{\Delta H_{\text{max, bot}}} \]
Electrodialysis

Electrodialysis is primarily used for brackish groundwater desalination. For salinities below 2,000 ppm, ED has sometimes been reported to have significantly lower energy consumption than RO for representative designs [77], but this advantage is lost as salinity increases. ED is also used in Japan to concentrate seawater to a nearly saturated brine (200,000 ppm) for salt making [78], and salt production by ED-RO hybrids has economic potential in other regions [48]. ED has seen renewed interest lately, with various new configurations nearing commercialization. For a 3,000 ppm feed, ED electrical energy consumption is roughly 0.8 kWh/m³ [41].

Separation in electrodialysis results from an electric field imposed across alternating cation and anion exchange membrane (Fig. 12). Chehayeb et al. have considered the entropy generation of ED [28, 79]. In this case, assuming locally isothermal conditions, Eq. (17) has the form

$$\sigma = \frac{1}{T} \mathbf{E} \cdot \mathbf{J} - \frac{1}{T} \sum_{k} \nabla_{T} \mu_{k} \cdot \mathbf{J}_{k}$$

(36)

The distribution of entropy generation between the membranes and flow channels within an ED stack depends greatly on the salinity of the liquid streams. For high salinities, most entropy production results from ohmic resistance in the membranes, but at low salinities most occurs within the liquid channels [79]. The entropy generation of a cell pair per unit area can be approximated for a 1-1 electrolyte (e.g., NaCl) as [28, App. B]

$$\dot{S}_{gen}'' \approx \frac{1}{T} \left( \Delta V_{cp} - \frac{\Delta \mu_s}{F} \right)$$

(37)

where \(\Delta V_{cp}\) is the voltage difference across a single cell pair and \(\Delta \mu_s\) is the difference in chemical potential between the salt in the concentrate channel and that in the dilute channel.

Chehayeb et al. [28] explored both counterflow and multistaging of ED as means to achieve lower entropy generation by equipartitioning. They found that the high fixed costs of ED usually encourage small membrane areas that come with high average current densities, so that the additional entropy generation associated with spatial imbalance does not contribute substantially to overall inefficiency. For those systems, equipartitioning provides little improvement in energy efficiency. However, if fixed costs can be lowered, so that greater membrane area is economically viable, multistaging could significantly reduce energy demand.

Forward osmosis

Forward osmosis systems use osmotic pressure differences across a membrane to draw water from a saline feed stream that has undesirable characteristics (e.g., scalants or waste products) into a draw stream of higher osmotic pressure having a simpler or more desirable chemistry. A second process, such as RO or a thermal separation, then removes the water from the draw stream. Hydraulic pressure differentials between the feed and draw streams are usually negligible.

FO has received significant attention in the past 15 years for its potential use in desalination, wastewater treatment, and...
pretreatment of feed water. Although FO seems unlikely to offer energetic advantages over direct desalination [80], its value in pretreatment and dewatering operations is well established [81]. FO appears to have reduced fouling compared to RO, although it is a misconception that this results from from the compaction of foulants by the higher hydraulic pressures of RO relative to FO [82].

The FO exchanger can be evaluated separately from the water-recovery process that follows it. The draw stream at high osmotic pressure flows counter to the feed stream at low osmotic pressure. From Eq. (32) for \( \Delta p \ll \Delta \Pi \), the entropy generation per unit FO membrane area is

\[
\dot{S}_{\text{gen}}^r = \frac{\bar{v}_w A}{T} (\Pi_{\text{draw}} - \Pi_{\text{feed}})^2
\]

Tow et al. [10] showed that the energy efficiency of forward osmosis exchangers could be improved by balancing the feed and draw stream mass flow rates so as to provide a uniform osmotic pressure difference between the counter-flowing streams. They provided analytical formulae for the second-law efficiency (Eq. 11) as a function of mass flow rates and other parameters, identifying a particular mass flow-rate ratio that maximized efficiency for given feed and draw inlet salinities and water recovery ratio (Fig. 13).

Summary

Entropy generation and discarded exergy in desalination systems directly raise the energy consumption of these increasingly important technologies. Desalination relies on mechanical, thermal, or electrical transport processes to separate pure water from saline water, and these transport processes dominate the entropy generation in desalination. By reducing gradients in temperature and concentration, and by making necessary gradients more spatially uniform, entropy generation can be minimized. System designs that recover thermal energy or flow work from leaving streams serve to reduce discarded exergy. Both approaches have guided substantial engineering improvements in the energy efficiency of desalination systems. Continued emphasis on the thermodynamic aspects of system-level design are likely to result in further improvements and should be the focus of research on energy efficient desalination.

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Nomenclature

\( A \) = Membrane permeability [mol m\(^{-2}\) bar\(^{-1}\) s\(^{-1}\)], or heat transfer area [m\(^2\)], by context
\( a_k \) = Activity of species \( k \)
\( c \) = Molar concentration [mol m\(^{-3}\)]
\( c_p \) = Specific heat capacity at constant pressure [J kg\(^{-1}\) K\(^{-1}\)]
\( D \) = Diffusion coefficient [m\(^2\) s\(^{-1}\)]
\( e_f \) = Flow exergy [J kg\(^{-1}\)]
\( E \) = Electric field vector [V m\(^{-1}\)]
\( F \) = Faraday constant, 96485.333 [C mol\(^{-1}\)]
\( g \) = Specific Gibbs energy [J kg\(^{-1}\)]
\( g_k \) = Molar Gibbs energy of pure solvent \( k \) [J mol\(^{-1}\)]
\( \dot{H} \) = Enthalpy flow rate [W]
\( h \) = Specific enthalpy [J kg\(^{-1}\)]
\( h_k \) = Molar enthalpy of species \( k \) [J mol\(^{-1}\)]
\( h_{ij} \) = Latent heat of vaporization [J kg\(^{-1}\)]
\( j_k \) = Flux vector of species \( k \) [mol m\(^{-2}\) s\(^{-1}\)]
\( J_Q \) = Heat flux vector [W m\(^{-2}\)]
\( J_O \) = Internal energy flux vector [W m\(^{-2}\)]
\( \bar{p} \) = Perimeter [m]
\( p \) = Hydraulic pressure [bar]
\( Q \) = Heat transfer rate [W]
\( R \) = Universal gas constant, 8.31446 [J mol\(^{-1}\) K\(^{-1}\)]
\( r \) = Recovery ratio, \( n_{\text{sep}}/n_{\text{inlet}} \)
\( S \) = Entropy [J K\(^{-1}\)]

\( \dot{S}_{\text{gen}} \) = Entropy generation rate [W K\(^{-1}\)]
\( \bar{s} \) = Specific entropy [J K\(^{-1}\) kg\(^{-1}\)]
\( \bar{s}_k \) = Molar entropy of species \( k \) [J K\(^{-1}\) mol\(^{-1}\)]

\[ \dot{S}_{\text{gen}}^r = \frac{\bar{v}_w A}{T} (\Pi_{\text{draw}} - \Pi_{\text{feed}})^2 \]

(38)

Tow et al. [10] showed that the energy efficiency of forward osmosis exchangers could be improved by balancing the feed and draw stream mass flow rates so as to provide a uniform osmotic pressure difference between the counter-flowing streams. They provided analytical formulae for the second-law efficiency (Eq. 11) as a function of mass flow rates and other parameters, identifying a particular mass flow-rate ratio that maximized efficiency for given feed and draw inlet salinities and water recovery ratio (Fig. 13).

\( W_{\text{pump}} \) = Pump work [W]
\( W_{\text{sep}} \) = Work of separation [W]
\( w_k \) = Mass fraction of species \( k \) [g kg\(^{-1}\)]
\( \mathbf{X} \) = Driving force vector for flux [units vary]
\( x \) = Position coordinate, varies by context [m]
\( z_k \) = Valence of species \( k \)

Greek letters and symbols

\( \Delta \) = Difference in a quantity, by context
\( \Delta V_{CP} \) = ED cell pair voltage difference [V]
\( \eta_{\text{II}} \) = Second-law efficiency of desalination plant, Eq. (11)
\( \mu_k \) = Chemical potential of species \( k \) [J mol\(^{-1}\)]
\( \Pi_k \) = Osmotic pressure of species \( k \) [bar]
\( \rho \) = Mass density [g m\(^{-3}\)]
\( \sigma \) = Volumetric entropy generation rate [W m\(^{-3}\)]
\( \nabla_T \) = Constant temperature gradient, see Eqs. (16) and (17)

Subscripts

\( 0 \) = Restricted dead state
\( a \) = Air
\( b \) = Brine
\( c \) = Cold stream
\( H \) = High temperature heat source  
\( h \) = Hot stream  
in = Inlet state  
\( k \) = Species \( k \)  
p = Product  
s = Salts  
sw = Saline water (feed)  
w = Water  

**Superscripts**  
\(*\) = Environment, or global, dead state  

**Acronyms**  
CFRO = Counterflow reverse osmosis  
ED = Electrodiagnosis  
FO = Forward osmosis  
GOR = Gained output ratio, Eq. (33)  
HCR = Modified heat capacity rate ratio, Eq. (35)  
HDH = Humidification-dehumidification  
MD = Membrane distillation  
RO = Reverse osmosis  

**Appendix A: Thermophysical Properties of Saline Water**  
The thermophysical properties of saline water differ from pure water, particularly the specific heat capacity, density, and vapor pressure. For seawater, the ionic composition is relatively uniform around the world, and extensive data sets and software libraries are available [84–86]. For brackish groundwater, the ionic composition varies significantly with location [30]; and for produced water (from drilling operations), the salinities can be far higher than seawater with highly variable compositions [87]. Both groundwater and seawater properties can be simulated using the Pitzer-Kim model [87]. Sodium chloride solution is sometimes used for simplified calculations [88, 89], but its properties differ somewhat from naturally occurring saline waters, especially in the absence of low solubility, scale-forming components.

**Appendix B: Entropy Generation in a Balanced Counterflow Heat Exchanger**  
For a balanced counterflow exchanger of length \( L \), \( T_e = T_{e,in} + ax \) where the constant \( a = (T_{e,out} - T_{e,in}) / L \). Integrating Eq. (18) for \( \Delta T \ll T_{e,out} \) gives Eq. (19):

\[
S_{gen} = \frac{U\delta T^2}{a} \int_0^L \frac{dx}{(T_{e,in} + ax)^2} = \frac{U\delta T^2}{a} \left( \frac{1}{T_{e,in}} - \frac{1}{T_{e,out}} \right) = \left( \frac{\delta T}{T_{e,in} - T_{e,out}} \right) \approx \left( \frac{\delta T}{T_{e,in} - T_{e,out}} \right) (B1)
\]

The “duty” of the process is the total flux transferred

\[
duty = \int_A J dA = \int_A L\Delta X dA = LA\cdot\overline{\Delta X} \quad (C1)
\]

where \( \overline{\Delta X} \) is the spatial average value of the driving force. The total rate of entropy generation, with Eq. (20), is

\[
S_{gen} = \int_A \int_0^\delta \sigma dA dx = \int_A \int_0^\delta X dAdx
\]

\[
= \int_A L(\Delta X)^2 dA = LA \cdot (\overline{\Delta X})^2 \quad (C2)
\]

When the driving force is uniform over the area, \( (\overline{\Delta X})^2 = \overline{\Delta X}^2 \). In this case of “equipartitioned forces,”

\[
S_{gen}' = LA \cdot (\overline{\Delta X})^2 = LA \cdot \overline{\Delta X}^2 = duty \cdot \overline{\Delta X} \quad (C4)
\]

For a given duty and LA, if distribution of the driving force is nonuniform, the entropy generation is greater than if the driving force were made uniform

\[
S_{gen} - S_{gen}' = LA \cdot (\overline{\Delta X})^2 > 0 \quad (C5)
\]

where the last step is a result of the Cauchy-Schwarz inequality. Several significant generalizations of the equipartitioning theorem are now in literature—see the discussion in Magnanelli et al. [25].

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