Desalination 386 (2016) 13–18

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Thermodynamic perspective for the specific energy consumption of seawater desalination

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HIGHLIGHTS

- Full thermodynamic perspective for work-driven and heat-driven seawater desalination
- Method-independent constrained thermodynamic bounds for specific energy consumption
- Understanding how and why desalination technologies fall short of fundamental limits
- Nature's thermal desalination scheme vis-à-vis commercial technologies

ARTICLE INFO

Article history:
Received 30 December 2015
Received in revised form 21 February 2016
Accepted 23 February 2016
Available online 2 March 2016

Keywords:
Specific energy consumption
Thermodynamic bound
Seawater desalination
Thermal desalination
Reverse osmosis desalination

ABSTRACT

The fundamental thermodynamic bound for the specific energy consumption (*SEC*) of seawater desalination is independent of mechanism and relates to work-driven processes (exemplified by reverse osmosis, RO). There is a corresponding method-independent *constrained* thermodynamic bound for heat-driven desalination, e.g., multi-effect and multi-stage flash distillation, along with thermal vapor compression. Similar constrained limits exist when the finite capacity of heat or work reservoirs must be accounted for. We elucidate basic insights and consequences of these mechanism-independent limits relative to the measured performance of the most efficient seawater desalination plants, specifically: (1) the dramatic differences in *SEC* between RO and thermal desalination as well as the degree to which each of them differs from their respective basic performance bounds, (2) the strikingly different dependence of the *SEC* of RO vs. thermal desalination on feedwater salinity and feedwater temperature, and (3) the magnitudes and sources of potential reductions in *SEC*. The *SEC* of nature's thermal desalination scheme (the solar-rainfall cycle) is also estimated.

1. Introduction

1.1. Unconstrained thermodynamic limit for work-driven desalination

Thermodynamics places a lower bound on the specific energy consumption (*SEC*) for desalination [1], which refers to the energy input per unit volume of desalted water produced, commonly in units of kWh/m^3. This fundamental limit is process-independent, and relates exclusively to the separation of solute from a solution of known temperature T and total ionic concentration C via a work-driven method (e.g., reverse osmosis, RO). Because energy consumption is often the major cost element in seawater desalination [2], *SEC* is generally a dominant – and certainly always a significant – consideration.

The unconstrained thermodynamic limit for desalination, SEC_o, is usually derived within the context of RO, and is equal to the solution's osmotic pressure Π which, for the dilute-solution condition valid for seawater, follows van't Hoff's Law:

$$SEC_o = \Pi = C\ R\ T \tag{1}$$

where R is the universal gas constant. At T = 300 K and a seawater salinity of 35 g/kg (principally NaCl), SEC_o = 0.76 kWh/m^3. Being a thermodynamic limit, Eq. (1) corresponds to reversible, dissipation-free operation. This in turn implies vanishingly small flux gradients through the system, which can only be realized in the limits of: (1) vanishing recovery ratio *RR* (the fraction of feedwater converted to desalted water), (2) an infinite number of stages, and (3) perfect energy recovery of brine pressure. Additional idealizations subsume negligible (a) pump inefficiency, (b) pressure-drop losses, (c) concentration polarization losses, (d) pressure and salinity in the permeate and (e) membrane fouling.

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http://dx.doi.org/10.1016/j.desal.2016.02.030
0011-9164/

1.2. Scope of the analysis

We restrict our attention to *seawater* desalination (1) because it is the overwhelmingly prevailing application, as opposed to brackish water or high-concentration solutions, and (2) in order to preserve a feasible scope for this paper.

For comparisons with actual systems, we confine consideration to the most efficient (lowest-*SEC*) work-driven and heat-driven desalination processes developed to date, because they minimize the contributions of dissipation deriving from technology-dependent and nominally process-unrelated sources (e.g., pre-treatment of feedwater, post-treatment of desalted water, pump inefficiencies, and low thermal conductance in heat exchangers). Namely, the most efficient systems should offer the best basis for comparison against thermodynamic limits. This in turn strengthens the likelihood that the respective method-independent limits can account for – and provide a broader understanding of – the dependence of the *SEC* of actual seawater desalination systems on key variables such as feedwater temperature, feedwater salinity, and recovery ratio (i.e., for the *relative* change in *SEC* for variations in each of these variables). A fringe benefit would be illuminating which measures could narrow the gap between actual performance and basic bounds, and by how much, as well as the thermodynamic wisdom of exploiting available heat by using it directly for thermal desalination, as opposed to first converting it to work (e.g., in low-temperature turbines) and then driving RO.

1.3. Basic trends and the Second Law

It might be asked whether a bound derived for RO desalination also pertains to *any* work-driven desalination strategy (independent of whether the input work is mechanical, electrical, chemical, or otherwise). The Second Law provides the answer, based on there being no restriction on the conversion efficiency from one form of work to another (since work carries no entropy). Hence every *work*-driven method must possess the same unconstrained thermodynamic limit of Eq. (1) (in the limit of dissipation-free, reversible operation).

A corollary of this observation answers the question of whether work-driven seawater desalination can benefit from pre-heating the feedwater. For RO, one motivation for hotter feedwater is lower viscosity, with the associated decrease in pumping energy. For other work-driven methods, such as capacitive deionization [3], the motivation could be assumedly superior efficiency due to higher ionic conductivity. But if system performance is not significantly hampered by dissipative pathways, then *SEC* must increase with *T*. Namely, although one aspect of the total energy balance may benefit from higher *T*, the net effect is that *SEC* must worsen as *T* rises.

1.4. Constrained work-driven desalination: recovery ratio

A *constrained* thermodynamic limit stems from requiring a non-vanishing recovery ratio $RR > 0$, which basically accounts for a finite-capacity work reservoir. For RO, that work reservoir is the available pressure difference, which can only be partially exploited. The limiting dependence of *SEC* on *RR* must be the same for all work-driven approaches (assuming a perfect energy-recovery device) — a functional dependence that can be established for RO as follows.

Reversibility means that the total available pressure difference is utilized in an infinite number of stages, with a local driving trans-membrane pressure that is vanishingly small. (In the heat-engine analysis for thermal desalination below, the analog is a vanishingly small local temperature difference along the heat exchangers.) The problem reduces to cascading an infinite number of stages each of which exploits an infinitesimal fraction of the total available pressure.

For a local permeate production $d(RR)$ (per unit volume of feedwater), the driving pressure $P(RR)$ increases by a factor of $1/(1-RR)$ relative to the known entry trans-membrane pressure $P(0)$. Since the maximum allowed conversion efficiency η_{conv} from one form of work to another is unity, $SEC(RR)$ is then:

$$\frac{SEC(RR)}{SEC_o} = \frac{\int_0^{RR} P\left(RR'\right)\eta_{conv} d\left(RR'\right)}{\int_0^{RR} P(0)\eta_{conv} d(RR')} = \frac{\int_0^{RR} \frac{P(0)}{1-RR'}\bullet 1\bullet d\left(RR'\right)}{\int_0^{RR} P(0)\bullet 1\bullet d(RR')} = -\frac{1}{RR}\ln(1-RR). \tag{2}$$

(Eq. (2) has been recognized previously, and derived in alternative fashions [4–6].)

The derivation of the more general relation for *SEC* as a function of *both RR and* the number of stages *N* is considerably more complex (even if the final formula is relatively simple), derived in [7] and plotted in Fig. 1:

$$\frac{SEC(RR,N)}{SEC_o} = \frac{N}{RR}\left(\frac{1}{(1-RR)^{1/N}} - 1\right). \tag{3}$$

Eq. (3) indeed approaches Eq. (2) as $N \to \infty$.

SEC for systems *without* energy recovery has also been derived [5,6] (including the general result for arbitrary *N* [3]), and is a factor of ~3–4 greater than *SEC* for RO systems *with* perfect energy recovery. We do not, however, belabor results for RO systems *without* energy recovery because (a) of the availability of commercial RO energy recovery systems with net conversion efficiencies as high as 97% [8,9], and (b) our focus is on systems as close to the basic performance limits as possible, hence with a minimal degree of avoidable irreversibilities.

Wherefore sizable *RR* values if minimal *SEC* can only be realized as $RR \to 0$? To boot, as can be confirmed from Eq. (3), as $RR \to 0$, $SEC \to SEC_o$ *independent* of *N*, so that the simplest and least costly option of a single stage would suffice. However, minimal *SEC* corresponds to vanishingly small desalted water flux, which is decidedly uneconomical. Cost factors unrelated to *SEC* shift system optimization to higher *RR* values [6]. A tradeoff exists, however, because *SEC* is also a rapidly increasing function of *RR*, not to mention the pragmatic problem of extensive salt deposition on the membranes and other system elements.

RO seawater desalination plants are typically designed for $RR \approx 0.35$–0.5 [1,8], which embodies an optimization subsuming the tradeoff among the costs of: energy, desalted water, maintenance, and system components. The (method-independent) limits of Eqs. (2)–(3) shed light on the affiliated compromise in efficiency:

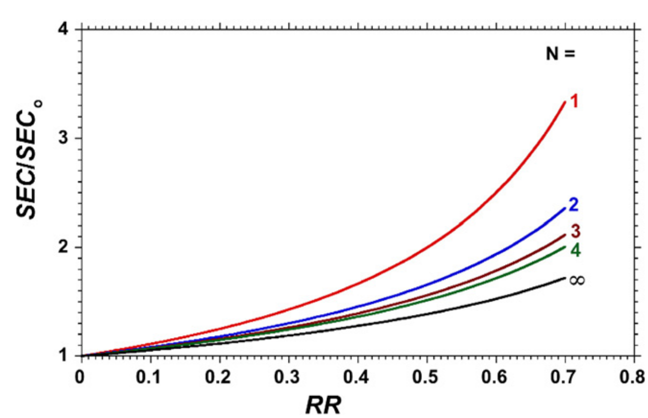

Fig. 1. Constrained thermodynamic limit for the *SEC* of RO systems (Eq. (3)) relative to its unconstrained limit SEC_o (Eq. (1)), as a function of recovery ratio *RR* for assorted values of the number of stages *N*. This illustration is limited to $RR < 0.7$ so as to relate to *SEC* values of practical interest.