



# Thermodynamic analysis of brine management methods: Zero-discharge desalination and salinity-gradient power production



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## HIGHLIGHTS

- ZDD and salinity-gradient energy were studied as brine management technologies.
- Minimum exergy for crystallization is below brine concentration for feed salinity < 100 g/kg.
- A reversible “blackbox” salinity-gradient power generation system was analyzed.
- Second Law efficiencies of crystallizer and brine concentrator were calculated.
- PRO system coupled with desalination can save about 0.42 kW h/m<sup>3</sup>.

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## ABSTRACT

Growing desalination capacity worldwide has made management of discharge brines an increasingly urgent environmental challenge. An important step in understanding how to choose between different brine management processes is to study the energetics of these processes. In this paper, we analyze two different ways of managing highly saline brines. The first method is complete separation with production of salts (i.e., zero-discharge desalination or ZDD). Thermodynamic limits of the ZDD process were calculated. This result was applied to the state-of-the-art industrial ZDD process to quantify how close these systems are to the thermodynamic limit, and to compare the energy consumption of the brine concentration step to the crystallization step. We conclude that the brine concentration step has more potential for improvement compared to the crystallization step. The second brine management method considered is salinity-gradient power generation through pressure-retarded osmosis (PRO), which utilizes the brine's high concentration to produce useful work while reducing its concentration by mixing the brine with a lower salinity stream in a controlled manner. We model the PRO system coupled with a desalination system using a detailed numerical optimization, which resulted in about 0.42 kW h/m<sup>3</sup> of energy saving.

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## 1. Introduction

Desalination produces a concentrated brine which has to be discharged back to the environment. Brine management has become a challenging task due to large increases in desalination capacity. In 2015, global desalination capacity reached 87 Mm<sup>3</sup>/day, of which 51 Mm<sup>3</sup>/day is seawater desalination. Figure 1 shows the growth of the global desalination capacity over recent years [1–6].

Seawater desalination has a recovery of roughly 50% [7], producing nearly equal flows of brine and product. Recovery varies greatly for the desalination of different feed waters, which makes it hard

to estimate the volume of brine discharge knowing only the treated water production rate. As a conservative estimate, over 50 Mm<sup>3</sup> of brine is discharged everyday. This large and growing quantity of brine should be managed with care in order to avoid harmful environmental effects.

One method of mitigating the environmental concerns from brine discharge is by avoiding discharge all together through the usage of zero-discharge desalination (ZDD) designs, which should be differentiated from zero-liquid discharge (ZLD) because ZDD does not even discharge salt. Near-ZDD designs have been implemented commercially for producing salt from seawater [8,9]. Economically feasible ZDD system designs for seawater desalination have also been proposed [10]. ZDD and ZLD systems broadly use two steps/sub-systems: a brine concentration step that concentrates the feed stream to near saturation conditions, and a crystallization step

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## Nomenclature

### Roman symbols

$a$	Activity
$A$	Membrane permeability, L/m <sup>2</sup> h bar
$A_m$	Membrane area, m <sup>2</sup>
$B$	Solute permeability coefficient, L/m <sup>2</sup> h
$D$	Diffusion coefficient, m <sup>2</sup> /s
$E$	Energy transfer per volume, kW h/m <sup>3</sup>
$f$	Friction factor
$g$	Specific Gibbs energy, J/kg K
$\bar{g}$	Partial molar Gibbs energy, J/mol K
$J$	Flux, L/m <sup>2</sup> h
$k$	Mass transfer coefficient, m/s
$M$	Molar mass, g/mol
MR	Mass flow rate recovery ratio of draw and feed streams
$\dot{m}$	Mass flow rate, kg/s
$\dot{N}$	Molar flow rate, mol/s
$q$	Specific heat transfer, kJ/kg
$Q$	Heat transfer, kW
$P$	Pressure, bar
Re	Reynolds number
RR	Recovery ratio
$s$	Salinity, g/kg
$S$	Structural parameter, $\mu\text{m}$
Sc	Schmidt number
Sh	Sherwood number
$T$	Temperature, °C
$v$	Velocity, m/s
$\dot{W}$	Work transfer, kW
$w$	Specific work transfer, kJ/kg

### Greek symbols

$\eta_{II}$	Second Law efficiency
$\eta_{\text{comp}}$	Compressor efficiency
$\dot{E}$	Exergy flow rate, kW
$\Pi$	Osmotic pressure, bar
$\Delta T_{\text{TTD}}$	Terminal temperature difference, K

### Subscripts

0	Ambient state
bc	Brine concentration
crys	Crystallization
b	Brine stream
d	Draw stream
desal	Desalination
power	Power production
f	Feed stream
H	Heat source
p	Pure water
in	Energy input to the system
m	Membrane surface
net	Net osmotic driving force (osmotic pressure-hydraulic pressure)
out	Energy output of the system
s	Salt
sat	Saturation
sw	Seawater stream

### Superscripts

least	Thermodynamic least work of separation
max	Thermodynamic maximum work of mixing
MVC	Mechanical vapor compression system
rev	Reversible system
sat	Saturated state

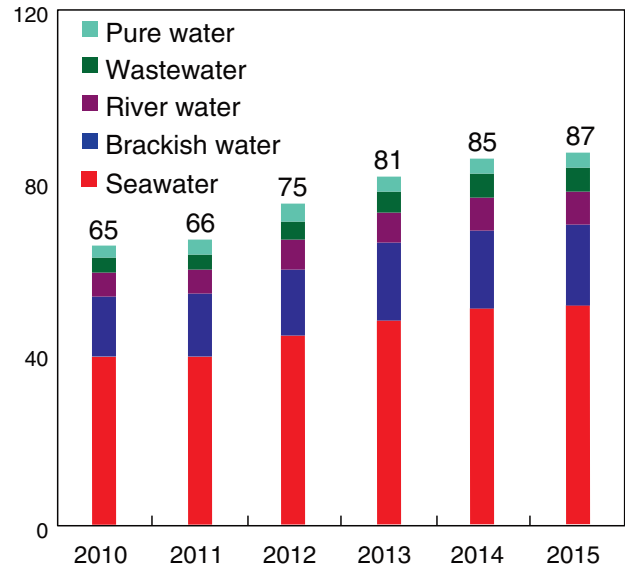


Fig. 1. Global desalination capacity based on the feed water type [1–6].

where saturated brine is completely crystallized. Several technology options exist for the brine concentration and crystallization steps. For the brine concentration step, the technologies that have been deployed industrially include: electrodialysis (ED) [8,9], mechanical vapor compression systems (MVC) [11–13], and solar evaporation ponds [11,14]. In Japan, electrodialysis (ED) has been used extensively for concentrating brine for salt production [8]. In such systems, incoming seawater feed is split into diluate and concentrate streams. The feed in the concentrate stream is typically concentrated from 35 g/kg to 200 g/kg while the diluate is diluted to slightly less than 35 g/kg and discharged back into the sea. ED systems are appropriate when partial desalination is an option [15]. For complete brine concentration producing pure product water, MVC systems are primarily used. The crystallization step in ZDD and ZLD is typically achieved through multi-effect evaporators [11] or solar evaporation ponds [11,14]. Apart from the above processes, newer processes such as SAL-PROC also exist where brine is sequentially crystallized using both evaporation and chemical processing [16]. More recently, membrane distillation (MD) has emerged as an alternative technology for an integrated brine concentration and crystallization process due to its ability to handle highly concentrated feed water [17–21].

Another method of handling brine discharge is to utilize the brine's exergy to produce power while lowering its salinity. This is done by using salinity-gradient power production technologies. Among these technologies, pressure-retarded osmosis (PRO) is believed to be the most promising technology because of its higher energy density [22,23] although efforts to improve technologies such as reverse electrodialysis (RED) are continuing [24,25]. In PRO, two flow streams at different salinities are introduced into a module where a semi-permeable membrane selectively rejects salt molecules. The more concentrated stream is commonly referred to as the draw stream and the less concentrated one as feed. Because of the chemical potential difference, osmosis occurs and water is drawn from the feed to the draw side. The draw stream is pressurized before being sent into the module which retards the osmosis (hence the name pressure-retarded osmosis). The applied pressure difference is smaller than the osmotic pressure difference so that osmosis is allowed to occur. The draw stream leaving the module is run through a turbine to produce power. The power produced by the system is net positive because the flow rate of the draw is higher at the outlet due to osmosis.

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