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Cost and energy needs of RO-ED-crystallizer systems for zero brine discharge seawater desalination

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Abstract

A zero brine discharge seawater desalination concept integrating reverse osmosis (RO), electro dialysis (ED) and crystallizer into a single system (REC) is presented. Analytical models were used to optimize parameters and minimize water production costs. Parameters varied were: the ratio of seawater to RO brine in the ED diluate channel, ED current density, ED diluate outlet salinity, electricity and salt prices, and RO recovery by adding high pressure RO (HPRO). Using only RO brine instead of only seawater in the ED diluate channel reduced water production costs by 87% from 27 to 3.5 \$/m³ while increasing salt production costs 26% from 135 to 170 \$/tonne-salt. The former was best for brine minimization, and the latter for salt production. Optimizing ED current density reduced REC costs by another 14% to 3.0 \$/m³ while increasing specific energy consumption 26% to 12.7 kWh_e/m³, corresponding to a Second Law efficiency of 18%. Adding an HPRO stage was uneconomical as it increased specific costs 21%. A salt price of 104.5 \$/tonne-salt will justify the cost of adding an ED-crystallizer. REC systems may be economically feasible in parts of the Middle-East. Producing other products such as Mg(OH)₂ or Br₂ may further improve economics.

Keywords: reverse osmosis, electro dialysis, hybrid, salt production, brine concentration, seawater

1. Introduction

Climate change and rapid population growth is causing rising water scarcity across the globe [1, 2]. Seawater desalination is increasingly being deployed to meet water demand around the world. As of 2017, around 55 million m³ of freshwater was produced by seawater desalination plants around the world [3] along with around 75 million m³ of saltier brine as a byproduct. Currently, seawater desalination brine is discharged back into the sea using outfalls. There is now a growing concern around the environmental impact of desalination plants especially the impact on marine life close to the plant intakes and outfalls [4, 5]. Countries especially in the Middle East in particular are considering more stringent regulations of the

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discharge of seawater desalination brine including potential zero discharge regulations. Policy makers and the industry have significant interest in understanding the technical and economic implications of zero brine discharge regulations.

To achieve zero brine discharge seawater desalination, three steps are necessary: desalination, brine concentration and crystallization of salts. Seawater RO has been shown to be the most energy efficient [6–12] and lowest cost [9, 13] method to desalinate seawater and produce freshwater. For the crystallization step, the state-of-the-art technology currently used are multi-effect evaporators [14]. In a previous work, some of the authors of this paper had shown that state-of-the-art crystallizers are more efficient than state-of-the-art brine concentrators and suggested that research work should focus on improving the brine concentration step [14]. For seawater brine concentration, two proven technologies that can be used are mechanical vapor compressors (MVC) systems [10, 15–18] and electrodialysis (ED) systems [19–26]. Chung et al. [14] had concluded that the potential for further efficiency improvements in MVC systems was limited. ED has been used for a wide range of applications: brackish water desalination [24, 27, 28], industrial water treatment [24, 29], heavy demineralization [30], in-home water treatment [31–33] and for the concentration of seawater for salt production [21–24, 26, 34]. Given the 50 years of industrial operational experience using ED for concentrating seawater [34], and given limited efficiency improvements possible in MVC [14], we focus the present paper on the potential ED has for cost reductions and efficiency improvements.

Several studies in the literature have proposed hybridizing RO with other desalination technologies for various reasons such as reducing water costs, energy consumption, membrane scaling or to better manage brine discharge [35–44]. Hybridizing RO with ED has been discussed previously for brackish water desalination [35, 38, 45–47], co-production of salt and water from seawater [36, 37, 48–52] and for industrial water treatment [41]. In 1996, Hayashi et al. [36] patented a concept of using RO, ED, an evaporator and relevant pre-treatment systems for producing both salt and water from seawater. In 2001, Ohya et al. [37] proposed a high-level concept using multi-ion adsorption columns, nanofiltration (NF), multi-stage RO, ED and an evaporator for producing water along with several salts and minerals. While potential revenue from all seawater derived products from a 1 million m³ seawater desalination plant was discussed, the authors did not discuss the specific energy consumption and the costs of the systems. However, Ohya et al. [37] identified where research and development efforts should focus to realize the concept.

In 2006, Davis [53] evaluated the economics of using RO, ED and evaporator systems for producing water, salt, bromine and magnesium hydroxide. Davis used literature data, industry sources, experimental setups and an analytical model to report the final capital and operating costs and product revenues for the concept. However, process model equations were not disclosed and the model could not be directly reproduced or verified. However, it was clear from Davis’s report that production of magnesium hydroxide and bromine were key to making the process profitable, with both products increasing profit margins 2.5 times than when

just water and sodium chloride were produced [53].

In 2012, Casas et al. [49] piloted a 500 L/hr ED plant to concentrate seawater RO (SWRO) brine to produce sodium chloride rich brine for the chlor-alkali industry and reported energy consumption, ED current densities and sodium chloride concentrations. Despite the RO brine being super-saturated in carbonate and sulfate salts, the presence of anti-scalants from the RO process and maintaining a pH of 5.5 inhibited scaling on the ED membranes. Jiang et al. [51] also carried out experiments on an ED stack treating SWRO brines comparing the performance of different ED membranes. Jiang et al. also reported on the water transport across the membranes under various conditions. Reig et al. [50] further established technical feasibility of using ED to concentrate SWRO brine through a pilot system, concentrating SWRO brine from 70 g/L of NaCl to 245 g/L of NaCl with the specific energy consumption varying between 120-190 kWh/tonne-NaCl as the current density was varied from 350-500 A/m². Reig et al. also determined that the specific energy consumption for producing 185 g/L of NaCl brine was lowest at a current density of 350 A/m². In 2015, Tanaka et al. [52] reported results from a computer simulation of ED treating desalination brine. The simulation was based on prior experimental investigations, and reported results for the specific energy consumption, ED current densities, voltages and the effect of linear flow velocity on performance.

In 2017, Thiel et al. [54] reviewed several methods to concentrate seawater RO brine and to produce sodium hydroxide from brine. The energetic advantages of using ED and partial desalination over complete desalination to concentrate brine was highlighted. A framework was also presented for calculating the thermodynamic least work of separation for sodium hydroxide production. In 2018, Du et al. [55], presented a process of using NF, ED, MVC, chemical softening, ion-exchange and an electrolyzer to produce sodium hydroxide from desalination brine. Du et al. had modeled the sub-systems using Aspen with the ED model being a black-box adaptation of a simple ED model developed by Nayar et al. [56] and reported energy consumption and operating costs.

While there have been several experimental studies and a few analytical model studies conducted on the RO-ED-crystallizer concept for producing salt and water from seawater, to the best of our knowledge, no study has reported the specific cost of an RO-ED-crystallizer system designed for zero brine discharge seawater desalination and evaluated the economics along with the energy needs of such a system. Furthermore, no study has looked at how the flow configuration and coupling between the RO and ED systems changes the costs. Inclusion of novel high pressure RO (HPRO) systems into the RO-ED-crystallizer concept have also not been considered in the literature on zero brine discharge desalination. In their previous work, some of the authors of this paper laid out the foundation for this investigation [56–58]. A preliminary simpler “zero-dimensional” ED model was made to ascertain the potential of the RO-ED-crystallizer concept [56]. The simpler model showed that the concept had promise, and topics for detailed investigation and modeling were outlined.

McGovern et al. [57] had conducted experiments on Neosepta AMX and CMX membranes characterizing salt and water transport across the membranes and used the data to modify a Nernst-Planck based ED model first reported by Fidaelo and Moresi [59]. McGovern et al. had verified the transport model against ED experiments conducted at various salinities simulating the use of multi-stage ED for treating high salinity produced water. This transport model was modified and adapted by Nayar et al. [58] for concentrating seawater, with the seawater brine concentration model validated against both experimental data from McGovern et al. [57] and industrial ED stack data obtained from a supplier [60]. Several industry representatives were contacted to verify cost numbers for key components [60–63]. While Nayar et al. [58] had evaluated a RO-ED-crystallizer concept for producing salt, the results were not directly transferable to the application of zero brine discharge desalination. The capacities of the systems for both applications are vastly different. We also realized that very different flow configurations were needed for the two applications. The effect of variations in flow configurations on system costs are described in detail in Section 3.

In this paper, we present a techno-economic analysis of integrating ED-crystallizers with a conventional large seawater RO desalination plant of 150,000 m³/day capacity. The difference in flow configurations when the focus is salt production as opposed to brine minimization is highlighted. The specific costs of the two configurations are reported in terms of both water and salt production. The specific energy consumed and the specific cost for a baseline RO-ED-crystallizer case are reported. The effect of varying ED diluate outlet salinity, current density and the addition of a HPRO stage on the system specific costs are also reported. An optimal configuration that lowers the specific cost of total water produced is reported. The effect salt prices have on the overall profitability of the concept is also discussed, along with the recommended direction for future research and development.

2. Methodology

In this paper, a techno-economic analysis of achieving zero brine discharge desalination using a RO-ED-crystallizer concept is presented. For our analysis, techno-economic models from Nayar et al. [58] for the RO, HPRO, ED and crystallizer systems are used. These models calculated the energy needs and costs, capital costs, membrane replacement costs, maintenance costs, chemical costs and labor costs. The models were previously validated and verified. The models used properties of seawater [64, 65] for the RO and HPRO models. For salinities greater than 120 g/kg since seawater properties were not available, we used the properties of aqueous sodium chloride as did McGovern et al. [57].

For all our analysis, we modeled a conventional large-scale seawater RO plant that took in seawater feed of salinity 35 g/kg. By looking at available plant operating data in the literature [66], we chose a representative seawater RO capacity of 150,000 m³/day, a single pressure stage RO design and energy recovery device based pressure recovery. Our analysis of available plant operating data [66] also showed that most seawater RO

plants around the world operated at a recovery of 42 %, which we held constant in our analysis as well. This resulted in an RO brine salinity of 60 g/kg in all cases discussed in this paper. The electricity price used for almost all the analysis work presented was 10 US cents/kWh_e. We further assumed a capacity factor, $\text{Cap}_{\text{factor}} = 0.9$, for the RO-ED-crystallizer system (i.e. the RO-ED-crystallizer is operational 90% of the time in a given year). The RO techno-economic model from Nayar et al. [58] was originally validated against data from DesalData for a capacity ranging from 250-2500 m³/day with the model deviating from DesalData’s water cost estimates by only 4.3-5.5 %. For a capacity of 150,000 m³/day, the only change we made to the model from Nayar et al. [58] was to the membrane replacement costs. At a capacity of 150,000 m³/day, membranes account for only 4.9 % of the cost instead of the 6.5 % used by Nayar et al. for smaller plants. With this change, our estimate for the cost of RO matched that of DesalData’s estimate for a 150,000 m³/day plant to within 9.5 %.

For accurately modeling the HPRO stage, minor adjustments to the HPRO model reported by Nayar et al. [58] had to be made to account for cost changes for components when the RO capacity is 150,000 m³/day. The specific capital cost of HPRO was only 1.03 times that of RO since the pressure dependent components only contributed to 28 % of the overall costs:

$$\text{SpCapEx}_{\text{HPRO,p,day}} = 1.03 \times \text{SpCapEx}_{\text{RO,p,day}} \quad (1)$$

where $\text{SpCapEx}_{\text{RO,p,day}}$ was reported as a function of RO capacity in Nayar et al. [58]. A more detailed breakdown of HPRO and RO costs can be found in Appendix B.

For the ED model, we used a target ED concentrate outlet salinity of 200 g/kg, representative of the limits of real-world ED systems [58]. The best available ED membrane data at high salinities from McGovern et al. [57] was used in our process model. The ED process model including its validation is described in more detail in Nayar et al. [58].

The crystallizer process and model we used is described in more detail and validated in Nayar et al. [58]. However, for the benefit of the readers we have summarized the crystallizer process and model here. Since real-world ED systems do not produce concentrate greater than 200 g/kg, crystallizers coupled with an ED system also have to concentrate the 200 g/kg brine to saturation before salt can be crystallized out and dried [58, 67]. The crystallizer here thus includes a multi-effect evaporator [58, 67], a de-watering unit and a dryer [58]. The multi-effect evaporator modeled was an electricity driven mechanical vapor recompression (MVR) based system. The cost and energy consumption of a conventional crystallizer system was sourced from a manufacturer [62] with the energy consumption validated against the literature [68] as well. Conventional crystallizers typically take in saturated brine. The model described in Nayar et al. [58] accounted for the fact that the crystallizer was taking in 200 g/kg brine. The model also accounted for the composition of the 200 g/kg brine to determine the amount of brine that must be purged from the crystallizer to ensure salt of

purity greater than 99.8 % .

To annualize capital costs, we used the same conditions for project life and rate of return as Nayar et al. [58] ($t_{\text{life}} = 20$ years and $r_{\text{return}} = 7$ %):

$$\text{CapEx}_{\text{year}} = \text{CapEx} \times \frac{r_{\text{return}}}{1 - \left(\frac{1}{1+r_{\text{return}}}\right)^{t_{\text{life}}}} \quad (2)$$

While the details of the models used can be found in Nayar et al. [58], for clarity we state a few terms here. In the RO-ED-crystallizer configuration, pure product water is produced at the RO sub-system, the crystallizer sub-system (see Fig. 1) and if it exists, the HPRO sub-system (see Fig. 11). The total water produced was thus:

$$\dot{V}_{\text{p, tot}} = \begin{cases} \dot{V}_{\text{p, RO}} + \dot{V}_{\text{p, crys.}}, & \text{without HPRO} \\ \dot{V}_{\text{p, RO}} + \dot{V}_{\text{p, HPRO}} + \dot{V}_{\text{p, crys.}}, & \text{with HPRO} \end{cases} \quad (3)$$

The recovery ratio (RR) of the RO system is defined as:

$$\text{RR}_{\text{RO}} = \frac{\dot{m}_{\text{p, RO}}}{\dot{m}_{\text{f, RO}}} \quad (4)$$

while the recovery ratio of the 2-stage RO-HPRO system is defined as:

$$\text{RR}_{\text{RO-HPRO}} = \frac{\dot{m}_{\text{p, RO}} + \dot{m}_{\text{p, HPRO}}}{\dot{m}_{\text{f, RO}}} \quad (5)$$

In all the analysis presented, RR_{RO} was 42 % and if a HPRO stage was present then $\text{RR}_{\text{RO-HPRO}}$ was 71 %. The costs of the systems were normalized to the total water produced to obtain the specific cost:

$$\text{SpCost}_{\text{system}}[\$/\text{m}^3] = \frac{\text{CapEx}_{\text{system, year}} + \text{OpEx}_{\text{system, year}}}{\dot{V}_{\text{p, tot, year}}} \quad (6)$$

Similar the specific energy consumed by the sub-systems was obtained by normalizing the energy consumed to the total water produced:

$$\text{SpEnergy}_{\text{system}}[\text{kWh}_e/\text{m}^3] = \frac{\dot{W}_{\text{system}} \times 1[\text{hr.}]}{\dot{V}_{\text{p, tot, hr}}} \quad (7)$$

Similarly, revenue from salt production was normalized to the water produced to obtain specific revenue:

$$\text{SpRev}_{\text{salt}}[\$/\text{m}^3] = \frac{\dot{m}_{\text{salt, year}} \times \text{Price}_{\text{salt}}[\$/\text{tonne}]}{\dot{V}_{\text{p, tot, year}} \times 1000[\text{kg}/\text{tonne}]} \quad (8)$$

Apart from analyzing system costs, we also calculated the Second Law efficiency of the RO-ED-crystallizer system, with the methodology used for least work analysis reported in Appendix A. The least work analysis

used in this paper was an adaptation of the method reported previously by Chung et al. [14].

3. Hybrid RO-ED flow configurations for zero brine discharge desalination and salt production

While several authors have studied the use of electro dialysis to concentrate reverse osmosis brine, to the best of our knowledge, no one has studied how the flow coupling between the RO and the ED system affects costs and the appropriateness of certain configurations for particular applications. In a previous work by some of the authors [58], an RO-ED configuration was presented for concentrating brine for salt production, where all of the RO brine was sent to the ED concentrate with seawater used as feed for the ED diluate stream. Typical ED based salt production plants use seawater feed as inlet for both streams. An intuitive next step by Nayar et al. [58] was that to maximize salt production, the concentrate salinity to the ED stream should be increased using an RO system. In the present paper, the effect of increasing the salinity of the diluate stream is explored.

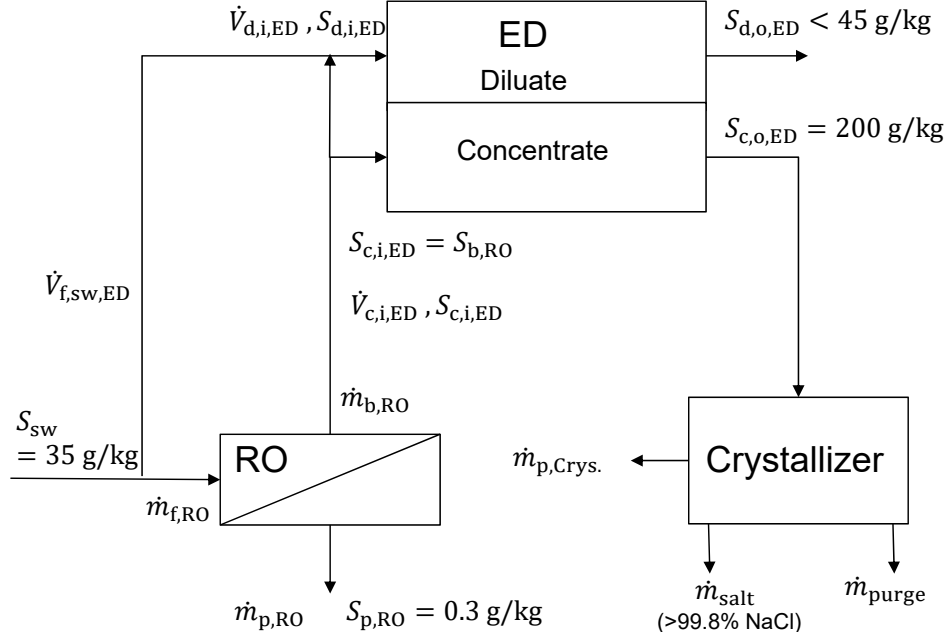


Figure 1: Flow diagram of a generic RO-ED-crystallizer configuration with seawater feed mixing with RO brine to form ED diluate.

A generic RO-ED-crystallizer system is shown in Fig. 1. Seawater comes in to an RO system generating pure product water (0.3 g/kg salinity, i.e., 300 ppm) and brine. The RO brine is split between the diluate and concentrate ED streams. A bypass line brings in additional seawater in to the diluate stream. The amount of seawater flowing to the diluate stream is characterized by the Seawater Diluate Ratio (SDR), defined as:

$$\text{SDR} = \frac{\dot{V}_{f,sw,ED}}{\dot{V}_{d,i,ED}} \quad (9)$$

The split between the diluate and concentrate streams is characterized by the Diluate Concentrate Ratio (DCR) defined as:

$$\text{DCR} = \frac{\dot{V}_{d,i,ED}}{\dot{V}_{c,i,ED}} \quad (10)$$

The diluate stream leaves the ED system at a concentration close to seawater salinity. The concentrate stream leaves the ED system at a salinity of 200 g/kg to a crystallizer system which produces pure product water, vacuum salt (99.8% pure) and a highly saline purge stream [58].

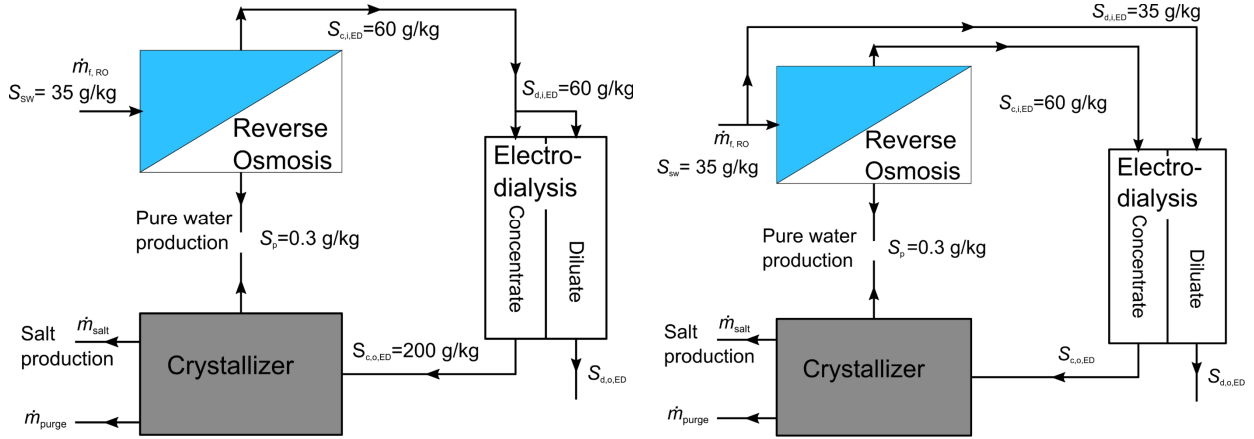


Figure 2: Flow diagram of an RO-ED-crystallizer with (a) $\text{SDR} = 0$ (i.e. no seawater feed in ED diluate) and, (b) $\text{SDR} = 1$ (i.e. all of the ED diluate is from seawater feed)

Figures 2 (a) and (b) show two extreme configurations of the generic design, representing designs with $\text{SDR} = 0$ and $\text{SDR} = 1$. The design with $\text{SDR} = 1$ was analyzed in detail by Nayar et al. [58] for salt production. To investigate the effects of SDR on cost and other parameters, we used the models of RO, ED and crystallizer systems previously reported by Nayar et al. [58]. For our analysis, we fixed the size of the seawater RO system at 150,000 m^3/day of product water, to represent a standard seawater desalination plant. We picked a seawater RO recovery ratio of 42% based on an analysis of seawater RO plants around the world [66]. The ED current density selected was 300 A/m^2 and a DCR of 80 matching a case validated against industrial data in Nayar et al. [58].

Figure 3 shows how the production of water from the RO system and the production of salt and water from the complete RO-ED-crystallizer system varied as SDR varied from 0 to 1. As the amount of seawater flowing in to the ED system was increased, both the overall salt produced and the water produced increased. Increasing the mass flow rate of seawater directly increased the amount of salt and water flowing from the diluate stream to the concentrate stream, with the ED diluate stream gradually becoming decoupled from the RO system. We have kept the DCR of the ED system fixed as we varied SDR , so increasing SDR meant that more of the RO brine was ending up in the ED concentrate stream. While we have held the water produced from the RO system constant, the increase in mass flow rate of brine to the crystallizer meant

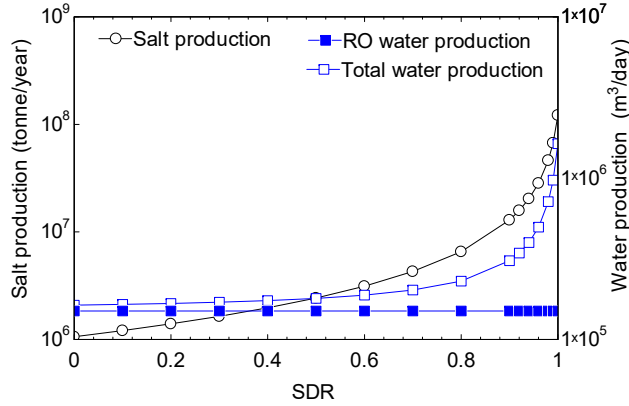


Figure 3: The production of water and salt from the RO-ED-crystallizer system varying with SDR for a fixed RO capacity of 150,000 m³/day.

that more water was also being produced as SDR was increased. Since both the water and salt produced increased with SDR, it is not directly obvious which SDR ratio was best for the application of zero brine discharge seawater desalination.

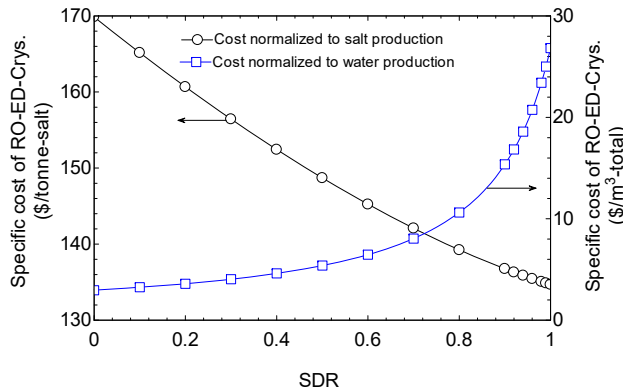


Figure 4: The specific cost of the RO-ED-crystallizer system per tonne of salt produced and per m³ of total pure water produced varying with SDR for a fixed RO capacity of 150,000 m³/day.

To identify the appropriateness of each flow configuration for various applications, the cost of the resulting RO-ED-crystallizer configuration was expressed as a specific cost in terms of both salt production and in terms of total water production. These specific costs varying with SDR are shown in Fig. 4. Clearly, with increasing SDR, the RO-ED-crystallizer system cost normalized to salt production decreases while the cost normalized to water production increases. An SDR = 0 translated to a system specific cost of \$ 170/tonne-salt and \$ 3/m³-water, while an SDR = 1 translated to a specific cost of \$ 135/tonne-salt and \$ 27/m³-water. Thus, if the primary market application is to produce salt, an RO-ED-crystallizer system must be operated as close to an SDR = 1, as possible. If the primary market need is water production,

and regulations require zero brine discharge, the RO-ED-crystallizer must be operated close to an $SDR = 0$. Several desalination plants are located near markets that also need salt, especially in the Middle East. For these plants, an SDR between 0 and 1 would make more sense. The specific SDR value needed would depend on local market conditions.

Apart from the cost of RO-ED-crystallizer systems, what is equally important is the amount of product water and salt produced. At an $SDR = 1$, the salt produced would be 107 million tonnes/year and the total water produced would be 1.6 million m^3 /day, when the RO system is fixed at 150,000 m^3 /day capacity. The maximum salt production at $SDR = 1$, if a typical seawater RO plant is hybridized with ED and a crystallizer, is around a third of global salt production. Thus, it follows that even from production amounts, an $SDR = 1$ is unreasonable for RO-ED-crystallizer based zero brine discharge seawater desalination. In Section 4.7, the relationship between production capacity and market feasibility is discussed in more detail.

4. RO-ED-crystallizer with $SDR = 0$ for Zero Brine Discharge Desalination

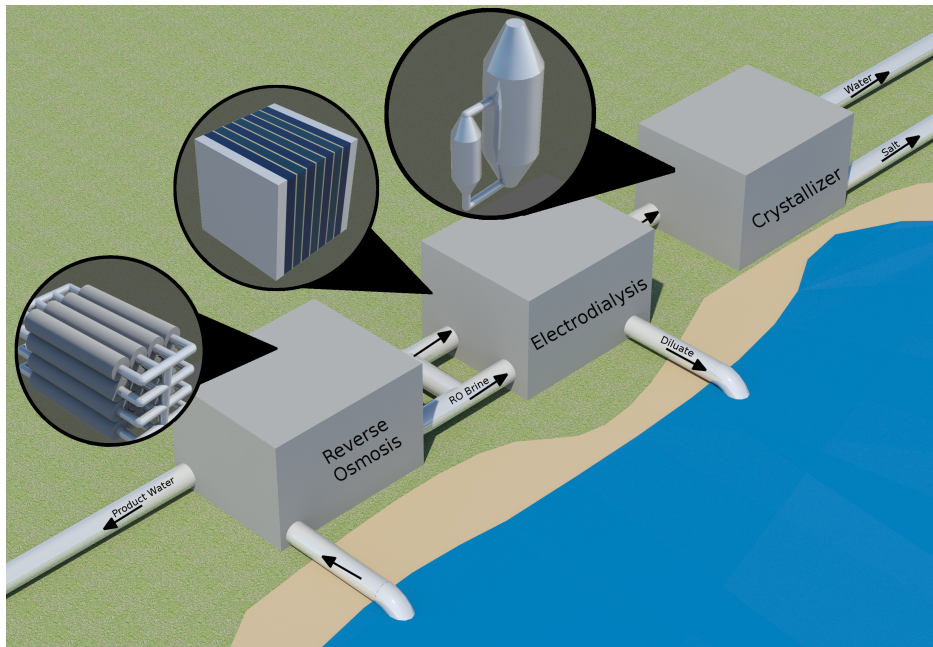


Figure 5: Zero brine discharge desalination plant with RO, ED and crystallizer sub-systems.

In this section we analyze the costs and energy requirements of a RO-ED-crystallizer with $SDR = 0$ for zero brine discharge desalination (shown in Fig. 5). First, the costs of a baseline case using conventional seawater RO and a conventional ED system are presented. From Nayar et al. [58], we know that current density affects costs more than other parameters, so we first find the optimal value of current density at $SDR = 0$. Next, the effect of extending the operation of RO to 120 bar and recoveries of 70% is explored.

Subsequently, we look at the effect of discharge limits on overall costs, the present the costs of an optimal RO-ED-crystallizer system with $SDR = 0$ and compare that with the potential revenue from salt production.

4.1. Baseline: Cost of conventional RO-ED-crystallizer based zero brine discharge desalination

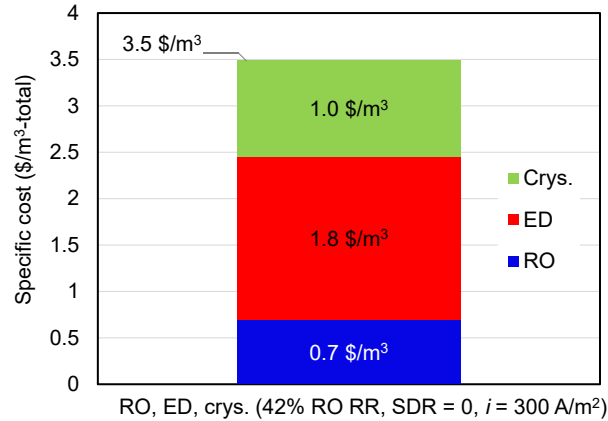


Figure 6: Specific cost of RO, ED and crystallizer sub-systems under conventional operating conditions (42 % RO recovery, 300 A/m^2 ED current density and 45 g/kg diluate outlet salinity).

Our analysis of the operational condition of seawater RO plants around the world showed that most seawater RO plants operated at a recovery of 42% taking in seawater at 35 g/kg, producing product water and discharging brine at 60.3 g/kg. As discussed in Nayar et al. [58], conventional seawater ED systems operate at around 300 A/m^2 current densities. For our baseline we chose an RO recovery of 42%, and an ED current density of 300 A/m^2 . A DCR value of 64 was selected to ensure the diluate stream was leaving at an acceptable salinity of 45 g/kg.

The cost and process models developed in Nayar et al. [58] were directly used to estimate the cost of the baseline case. Figure 6 shows the calculated specific costs for the RO, ED and crystallizer systems normalized to the total water produced by the RO and crystallizer systems. The RO system had a specific cost of 0.7 $\text{\$/m}^3$ of total water produced while the ED system had a specific cost of 1.8 $\text{\$/m}^3$ and the crystallizer system had a specific cost of 1.0 $\text{\$/m}^3$. In terms of a ratio of cost of ED and crystallizer to the RO system costs, the ED was 2.5 times the cost of the RO system, and the crystallizer was 1.5 times the cost of RO. Cumulatively a conventional RO-ED-crystallizer system had a specific cost of 3.5 $\text{\$/m}^3$, 5 times more than a conventional seawater RO system. The additional water produced by the crystallizer in a configuration of $SDR = 0$ was only 10 % of that from the RO sub-system, so these specific cost figures can be approximated in terms of $\text{\$/m}^3$ of RO product water as well. Clearly, achieving zero brine discharge through conventional operation of an RO-ED-crystallizer system is expensive.

We also looked at the specific energy consumed by each sub-system in the baseline case (Fig. 7). The RO system consumed 2.0 kWh_e/m^3 of total water produced, while the ED system consumed 1.9 times more

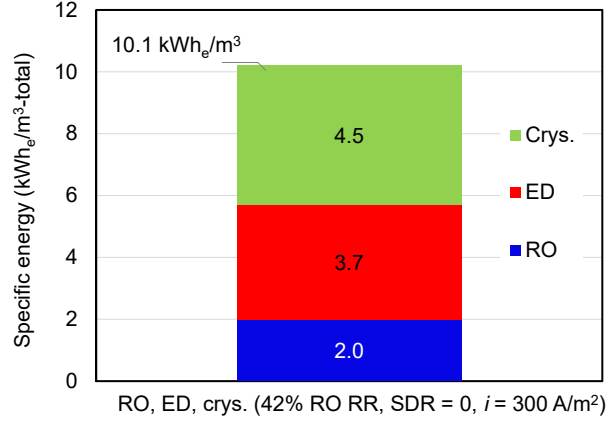


Figure 7: Specific energy consumption of RO, ED and crystallizer sub-systems under conventional operating conditions (42 % RO recovery, 300 A/m^2 ED current density and 45 g/kg diluate outlet salinity).

energy at $3.7 \text{ kWh}_e / \text{m}^3$ and the crystallizer system consumed 2.3 times more energy at 4.5 kWh_e per m^3 of total water produced. The complete RO-ED-crystallizer system under conventional operating conditions consumed $10.1 \text{ kWh}_e / \text{m}^3$ of specific energy, 5.1 times more than a conventional seawater RO system. Thus, achieving zero brine discharge desalination using a RO-ED-crystallizer system requires significantly more energy than a standalone seawater RO system.

In the next sub-sections we look at how and to what extent the RO-ED-crystallizer system costs can be further reduced.

4.2. Optimizing ED diluate outlet salinity significantly reduces costs

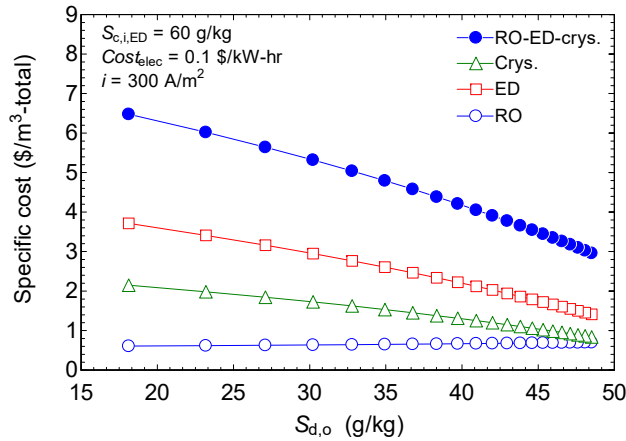


Figure 8: Specific cost of RO, ED, crystallizer and RO-ED-crystallizer varying with ED diluate outlet salinity (300 A/m^2 ED current density, 42 % RO recovery and electricity price of 10 US cents/kWh_e).

Figure 8 shows how the specific cost of the RO, ED, crystallizer sub-systems and the total RO-ED-crystallizer system varies with the salinity of the ED diluate outlet, a proxy for brine discharge limits. The

seawater RO sub-system is operated at an RR of 42 % corresponding to an RO brine salinity (and ED inlet salinity) of 60 g/kg, the ED sub-system is operated at a current density of 300 A/m², the ED concentrate leaves at a salinity of 200 g/kg, and the electricity price is 10 US cents/kWh_e. While the RO cost remained constant, both the ED and crystallizer costs reduced as the ED dilute outlet salinity was increased. For a given amount of 60 g/kg brine flowing in to an ED system under fixed average current density (i.e., fixed driving force) and fixed concentrate outlet, increasing the salinity of the ED diluate outlet implies that an increase in the flow rate of the diluate going to the ED stack (i.e., more salt needs to go in to the diluate stream for more salt to come out of the diluate stream). This means that the DCR increases with the discharge limit — higher the discharge limit, higher the DCR. This translates to a reduced flow rate of concentrate going into the ED stack and a reduced flow rate of concentrate leaving the ED stack — reducing the ED membrane area and the crystallizer capacity. For ED diluate outlet salinities of 20 g/kg, 35 g/kg and 45 g/kg, the corresponding specific cost of a RO-ED-crystallizer system was 6.3, 4.8 and 3.5 \$/m³ of total water produced. Thus, increasing the ED diluate outlet salinity from 35 g/kg to 45 g/kg alone reduced RO-ED-crystallizer specific costs by 27 %.

For ensuring that the analysis presented in this paper is applicable for a wide range of applications around the core RO-ED configuration, we chose a ED dilute outlet salinity of 45 g/kg. This reduces the specific costs with limited environmental impact. Brine at 45 g/kg can easily be diluted down to 35 g/kg with the help of relatively inexpensive outfalls. Furthermore, if complete zero liquid discharge norms are in place, this stream could be re-circulated back to the RO inlet after softening and removing divalent ions using nanofiltration (NF) [69, 70] or other means. Several configurations can be envisioned around the basic RO-ED configurations and operating parameters presented in this paper.

4.3. Increasing ED current density reduced system costs 14 %

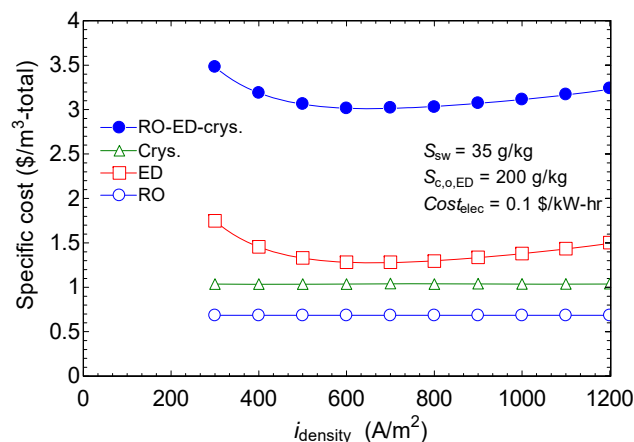


Figure 9: Specific cost of RO, ED, crystallizer and RO-ED-crystallizer varying with current density.

In Nayar et al. [58], for an RO-ED-crystallizer system of SDR = 1 and fixed DCR, increasing ED current

density from 300 A/m² to 600 A/m² reduced the specific cost of salt production by 21 %. For an SDR = 0, we expect a similar trend. For our analysis we kept the RO capacity at 150,000 m³/day, the RO recovery at 42%, a DCR value was chosen to keep the ED diluate salinity at around 45 g/kg and the ED current density was varied.

Figure 9 shows the specific cost of the RO, ED and crystallizer sub-systems and that of the RO-ED-crystallizer system varying with ED current density. While the ED specific costs reduced until 600 A/m², the RO and crystallizer specific were constant. Keeping the ED diluate outlet salinity fixed kept the ED concentrate outlet the same ensuring that the crystallizer capacity did not vary. Thus, the total RO-ED-crystallizer cost kept reducing until an ED current density of 600 A/m². The overall cost reduced from 3.5 \$/m³ of total water produced to 3.0 \$/m³ as the ED current density was increased from 300 A/m² to 600 A/m² — a cost reduction of 14 %.

4.4. Optimizing ED current density based on electricity prices

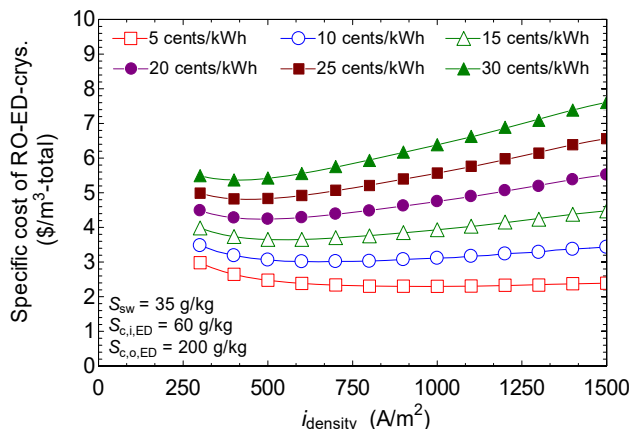


Figure 10: Specific cost of RO-ED-crystallizer varying with current density and electricity prices (42 % RO recovery).

The optimal ED current density is a function of electricity prices. We varied electricity prices from 5 to 30 US cents/kWh_e, and analyzed how the specific cost of an RO-ED-crystallizer system (SDR = 0) varied with current density. Figure 10 shows the results. The optimal ED current densities for an electricity price of 5, 10, 15, 20, 25 and 30 US cents/kWh_e were 800, 600, 550, 450, 450 and 400 A/m².

4.5. Hybridizing using HPRO to achieve 71% recovery and 120 bar operation increased the specific cost of water by 21 %

For the application of salt production where SDR was 1, hybridizing RO to 120 bar led to a 7 % reduction in RO-ED-crystallizer costs with additional revenue from water production [58]. In this section we investigated the effect of further hybridizing RO with ED using a 2-stage configuration with the addition of a high pressure RO (HPRO) stage that operated up to 120 bar pressure bringing the total RO-HPRO recovery

to 71%. Unlike Nayar et al. [58], the SDR of the RO-ED-crystallizer here is 0, with all of the HPRO brine at 120 g/kg salinity going to the ED system. Figure 11 shows the RO-HPRO-ED-crystallizer configuration we modeled.

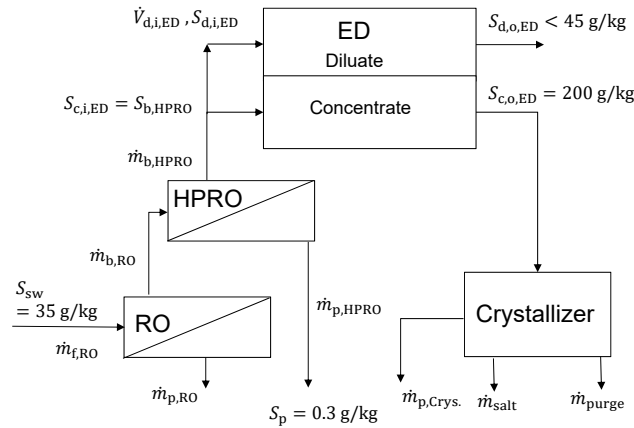


Figure 11: Flow diagram of a RO-HPRO-ED-crystallizer configuration with seawater with HPRO brine flowing in to the diluate and concentrate streams of the ED sub-system.

For our analysis of the RO, HPRO, ED and crystallizer systems, we used the same cost and process models from Nayar et al. [58]. The detailed analysis of the cost model for the HPRO system is given in Appendix B. Even with the cost additions due to the need for higher pressure piping, pumps, pressure vessels and membranes, the cost of the HPRO system was found to be only 1.03 times higher than the cost of the RO system (1258 \$-day/m³ for an additional 150,000 m³/day HPRO stage against 1219 \$-day/m³ for a conventional seawater RO plant of the same size).

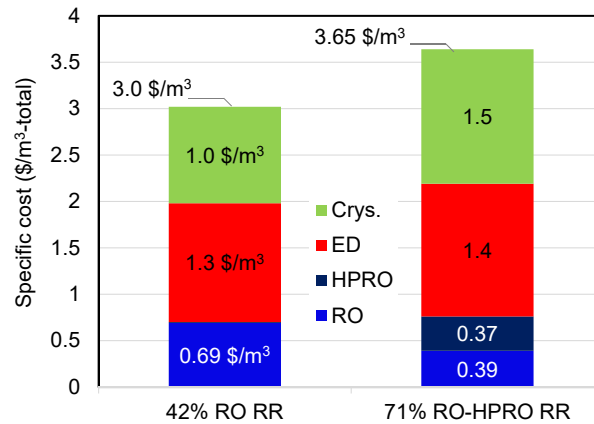


Figure 12: Comparison of specific costs of a RO-ED-crystallizer with a conventional 42 % RR RO against an RO-ED-crystallizer with a 2-stage RO system (RO followed by HPRO) with a 71 % RR for the RO-HPRO component.

Figure 12 shows the results comparing the specific cost for the two RO-ED-crystallizer designs: a 42 % RR conventional seawater 1-stage RO plant integrated with an ED and crystallizer system against a 71 % RR

Table 1: Relevant plant parameters for a RO-ED-crys. system with and without a HPRO stage

Plant parameter	Value
<i>Without HPRO stage</i>	
RO RR	42 %
RO water prod.	150,000 m ³ /day
Crys. water prod.	14,777 m ³ /day
Total water prod.	164,777 m ³ /day
Total salt prod.	3555 tonnes/day
Total annual salt prod.	1,167,817 tonnes/year
Specific energy (total)	12.7 kWh _e /m ³
Specific cost (total)	3.0 \$/m ³
<i>With HPRO stage</i>	
RO-HPRO combined RR	71 %
Total water prod.	252,377 m ³ /day
Total salt prod.	8735 tonnes/day
Total annual salt prod.	2,869,597 tonnes/year
Specific energy (total)	15.6 kWh _e /m ³
Specific cost (total)	3.65 \$/m ³

RO-HPRO (2-stage RO) plant integrated with an ED and crystallizer system. Table 1 reports the relevant performance data for both the cases. While the salinity of the inlet to the ED system in the former was 60 g/kg, in the latter it was 120 g/kg. While in Nayar et al. [58], increased hybridizing of RO (i.e. increasing RO brine salinity) led to reduced costs, here, the overall specific costs actually increased. For both cases, we kept the ED current density at an optimized value of 600 A/m² and picked a DCR value that ensured that the salinity of the ED dilute outlet was 45 g/kg.

The RO-ED-crystallizer with the 1-stage RO system cost 3.0 \$/m³ of total water produced while the one with the HPRO system cost 3.65 \$/m³ — an increase of 21 %. While the specific capital cost of the HPRO system was only 3 % higher than that of a standalone conventional seawater RO system, the total specific cost of the RO-HPRO system was about 16 % higher than that of a standalone RO system. The high operating costs of the HPRO system was the main reason for this. What we did not expect however, was a marginal increase (8 %) in the ED costs and a significant increase (50 %) in the crystallizer costs. The presence of the HPRO system providing brine at 120 g/kg drastically increased the amount of 200 g/kg concentrate produced by the ED system, more than doubling the crystallizer size and the amount of salt produced. Furthermore, setting the ED dilute outlet salinity to 45 g/kg required the ED system to do additional work and required more membrane area to take 120 g/kg brine to 45 g/kg than the case of taking 60 g/kg brine to 45 g/kg. With the addition of the HPRO stage, the total specific energy consumption of the RO-ED-crystallizer also increased from 12.7 kWh_e/m³ to 15.6 kWh_e/m³ — an increase of 23 %. This is shown in Fig. 13.

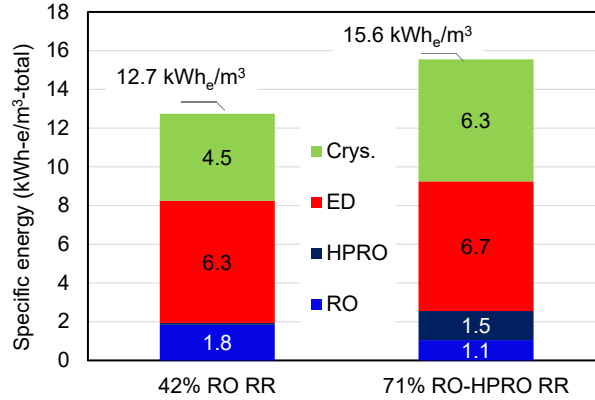


Figure 13: Comparison of specific energy consumption of a RO-ED-crystallizer with a conventional 42 % RR RO against an RO-ED-crystallizer with a 2-stage RO system (RO followed by HPRO) with a 71 % RR for the RO-HPRO component.

Clearly, there is no incentive of cost reductions to increase the hybridization of RO with the ED system. However, an HPRO system may be added to the RO-ED-crystallizer design to increase salt or water production from an existing seawater RO plant. Adding an HPRO stage increased water production 0.53 times from around 164,777 m³/day to 252,377 m³/day, and increased the production of salt 1.36 times from 3555 tonnes/day to 8735 tonnes/day.

Antiscalants can mitigate the scaling potential in HPRO stage:

In Nayar et al. [58], a detailed discussion on the risks of scaling in the HPRO stage from a high concentration of divalent ions was presented. For the benefit of the readers here, we summarize the key results here. An analysis of the estimated brine composition leaving the HPRO stage showed that the brine was saturated in calcium sulfate and calcium carbonate. However, working with an antiscalant company [71] with operational experience with seawater, we were able to determine the right antiscalant product and dosage with which the scaling risk could be mitigated. We found that this aligns with conventional industrial practice where antiscalants are used by seawater RO plants around the world to operate while generating RO brines saturated in scale forming salts. However, to be sure, laboratory experiments need to be conducted on a small scale RO-HPRO system to verify the efficacy of antiscalants.

Nanofiltration pre-treatment, if used, can be more expensive than RO and RO-HPRO:

We determined that with use of the appropriate antiscalants, an HPRO stage that could deliver a total RO-HPRO recovery of 71 % without the need for nanofiltration (NF) based pre-treatment to remove divalent ions. However, NF pre-treatment can be used for other purposes such as: enabling the recovery of calcium and magnesium salts from seawater, reducing crystallizer maintenance costs, increasing the salt purity from the crystallizer etc. During the course of study, we realized that NF pre-treatment costs had not been widely reported in the literature. Thus, for the benefit of readers we evaluated an approximate upper bound to the cost of NF pre-treatment. While NF may not be needed to operate the HPRO stage, it could enable the

recovery of calcium and magnesium salts from seawater desalination. The cost model and process model for NF we used was previously reported in Nayar et al. [58]. The model was applied to the zero brine discharge case with the key results presented here. The use of NF is discussed in more detail in Appendix C.

An NF pre-treatment system added before the RO-HPRO-ED-crystallizer system to treat a 100 % of the RO feed, with the NF recovery being 70 %, will add a specific cost of around 0.53 $\$/\text{m}^3$ of total water produced. For reference, if there were no HPRO stage, the NF system would have added a specific cost of around 0.94 $\$/\text{m}^3$ of total water produced. On a permeate production basis, the specific capital cost of an NF system and a RO system cost were quite similar. However, due to the larger amount of feed water going to the NF system, an NF system treating 100 % of RO feed was overall more expensive than the RO system itself.

Overall, for the application of zero brine discharge desalination using an RO-ED-crystallizer, without the strategic need for producing more water or salt from an existing seawater RO facility, we do not recommend further increasing the recovery of the RO system using an additional HPRO stage.

4.6. Optimal RO-ED-crystallizer design

4.6.1. Specific costs

Table 2: Summary of cost reducing (or increasing) steps taken and the associated RO-ED-crystallizer specific cost reductions. The last two columns show the cost reduction (or increase) corresponding to each step expressed in $\$/\text{m}^3$ of total water produced and as a percentage reduction with respect to the previous step.

Case	System	Cost reducing step	SpCost ($\$/\text{m}^3$)	ΔSpCost ($\$/\text{m}^3$)	ΔSpCost (%)
1	RO-ED-crys.	Nayar et al. [58] config., SDR = 1	\$ 27	\$ -	0%
2	RO-ED-crys.	Baseline: Optimizing SDR, SDR = 0	\$ 3.5	\$ 23.5	87%
3	RO-ED-crys.	Optimizing i , $i = 600 \text{ A/m}^2$	\$ 3.0	\$ 0.5	14%
4	RO-HPRO-ED-crys.	<i>Adding HPRO to case 3</i> Adding HPRO stage	\$ 3.65	\$ -0.65	-21%
3	RO-ED-crys.	<i>Most optimal case: Case 3</i> Optimizing i , $i = 600 \text{ A/m}^2$	\$ 3.0		

Table 2 summarizes the cost reduction steps taken, the costs of the associated RO-ED-crystallizer systems, and the cost reductions (or increases) in each step considered. The key design choices that reduced costs for a zero brine discharge desalination application were: choosing an SDR of 0 instead of SDR of 1, choosing a ED diluate outlet salinity that reduced costs, optimizing current density based on electricity prices, and choosing not to further hybridize RO with ED through a HPRO stage.

For an electricity price of 10 US cents/kWh_e, the cost of an RO-ED-crystallizer system for zero brine discharge desalination is minimized at an SDR of 0, an ED diluate outlet salinity of 45 g/kg, ED current

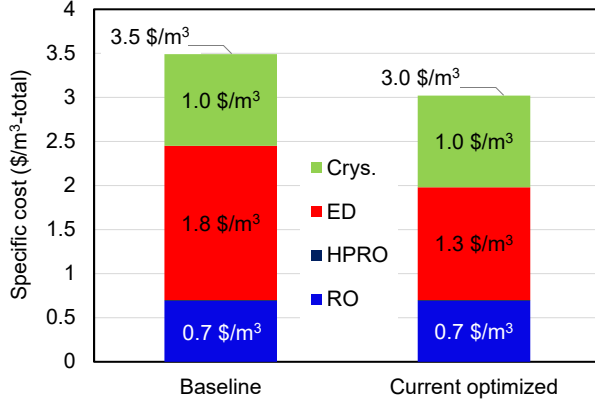


Figure 14: Comparison of specific costs of a current density optimized RO-ED-crystallizer (case 3 in Table 2) with the baseline case (case 2 in Table 2).

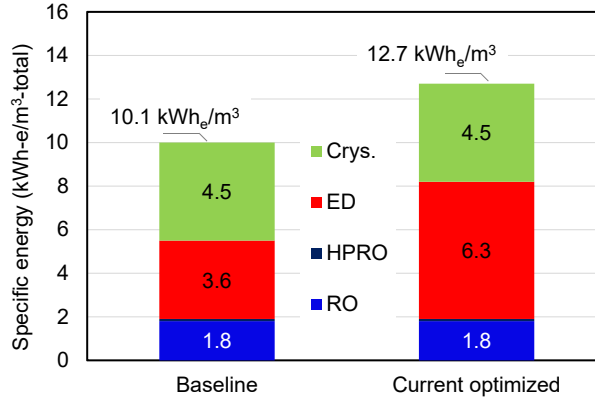


Figure 15: Comparison of specific energy consumption of a current density optimized RO-ED-crystallizer (case 3 in Table 2) with the baseline case (case 2 in Table 2).

density of 600 A/m^2 and with a 1-stage RO system with recovery 42 % (i.e. without a HPRO stage). Shifting from the $\text{SDR} = 1$ RO-ED-crystallizer design in Nayar et al. [58] to $\text{SDR} = 0$ here, reduced costs 87 %, from $27 \text{ \$/m}^3$ to $3.5 \text{ \$/m}^3$. Increasing ED current density from 300 A/m^2 to 600 A/m^2 further reduced costs another 14 % from $3.5 \text{ \$/m}^3$ to $3.0 \text{ \$/m}^3$. Further hybridizing with RO through adding a HPRO stage was not done as it would have increased costs 21 %.

Figure 14 compares the results of the specific cost of the baseline RO-ED-crystallizer system against the cost optimized design.

4.6.2. Specific energy consumption

Figure 15 compares the specific energy consumption of the of the baseline RO-ED-crystallizer system against the cost optimized design. While the baseline case consumed $10.1 \text{ kWh}_e/\text{m}^3$, the optimized case consumed more energy at $12.7 \text{ kWh}_e/\text{m}^3$ — a specific energy increase of 26 %. This is expected since the

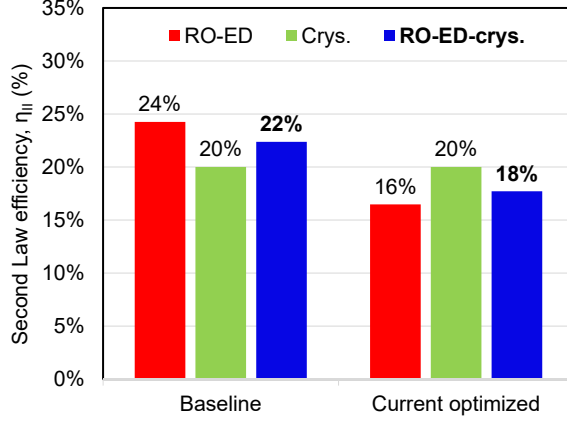


Figure 16: Comparison of Second Law efficiency of a current density optimized RO-ED-crystallizer (case 3 in Table 2) with the baseline case (case 2 in Table 2).

specific cost reductions were achieved by increasing the current density.

To put the specific energy consumption values in to perspective, we compared the specific energy consumption of the optimal RO-ED-crystallizer representing “partial desalination” against the specific energy consumption of state-of-the-art MVC-crystallizer based zero liquid discharge systems that completely separated seawater to salt and water. The specific energy consumption for a combined 1-effect MVC brine concentrator and multi-effect evaporator crystallizer system calculated from data reported by Chung et al. [14] was 23.8 kWh_e/m³ of total water produced. If a 2-effect MVC brine concentrator was used instead of a 1-effect MVC system, the value would have been 19.8 kWh_e/m³. Thus, the specific energy consumption of an optimal RO-ED-crystallizer implementing “partial desalination” was 36-46 % lower than that of state-of-the-art complete zero liquid discharge systems reported by Chung et al. [14].

4.6.3. Second Law efficiency

Figure 16 compares the Second Law efficiency of the baseline RO-ED-crystallizer system against the cost optimized design, with the method used to calculate the Second Law efficiency described in Appendix A. Since the energy consumption was increased to reduce costs, the Second Law efficiency of the cost optimized RO-ED-crystallizer was lower than that of the baseline case. The Second Law efficiency of the final cost optimized RO-ED-crystallizer was 18 %. In the cost optimized design, the RO-ED brine concentration step had an efficiency of 16 % while the crystallizer had an efficiency of 20 %. For comparison, Chung et al. [14] had reported Second Law efficiencies of 11.6 % and 24.4 % for a 2-effect MVC brine concentrator and a multi-effect evaporator crystallizer. The hybrid RO-ED system was more efficient than a 2-effect MVC system. It must be noted that the least work of brine concentration was also lower for the RO-ED system than the least work for the MVC system because of the presence of the ED diluate stream which enabled “partial desalination” in the RO-ED case (see Appendix A). The crystallizer in our analysis had a lower

efficiency than that in Chung et al. because our crystallizer had a feed stream with a much lower salinity at 200 g/kg and because our analysis accounted for a purge stream. In comparison, the crystallizer analyzed by Chung et al. had a feed salinity of 250 g/kg and the analysis there did not include a purge stream.

4.7. Effect of revenue from salt production

Table 3: Reductions to the specific cost of an optimal RO-ED-crystallizer from salt revenue at select salt prices. The last two columns show the cost reduction corresponding to each salt price expressed in $\$/\text{m}^3$ of total water produced and as a percentage reduction with respect to the baseline case.

Case	System	Cost reducing step	SpCost (\$/m ³)	Δ SpCost (\$/m ³)	Δ SpCost (%)
3	RO-ED-crys.	<i>Baseline: Most optimal case, Case 3</i> SDR = 0, 42 % RO RR and $i = 600 \text{ A/m}^2$	\$ 3.0		
		<i>Adding salt revenue to the baseline</i>			
3a	RO-ED-crys.	Salt price at \$ 10/tonne-salt	\$ 2.8	\$ 0.2	7%
3b	RO-ED-crys.	Salt price at \$ 20/tonne-salt	\$ 2.6	\$ 0.4	14%
3c	RO-ED-crys.	Salt price at \$ 30/tonne-salt	\$ 2.4	\$ 0.6	21%
3d	RO-ED-crys.	Salt price at \$ 50/tonne-salt	\$ 1.9	\$ 1.1	37%
3e	RO-ED-crys.	Salt price at \$ 104.5/tonne-salt	\$ 0.76	\$ 2.26	75%
3f	RO-ED-crys.	Salt price at \$ 140/tonne-salt	\$ 0.0	\$ 3.0	100%

The specific cost of the RO-ED-crystallizer is only one aspect. We must also consider the potential of generating revenue from the brine. For the purposes of this paper, we only evaluate the economics of producing salt (i.e. sodium chloride) and not other components. There are two aspects to be considered here: the price of salt and the volume of salt needed by the market.

First, we consider the salt production capacity from a seawater RO plant fitted with a RO-ED-crystallizer. A 150,000 m³/day seawater RO plant integrated with an ED and crystallizer optimized an electricity price of 10 US cents/kWh_e will produce 3555 tonnes/day of salt which is 1.17 million tonnes/year (see Table 1). Most vacuum salt plants produce between 0.4 to 1.2 million tonnes/year of salt [63]. Thus, the salt production capacity in an integrated zero brine discharge RO-ED-crystallizer design is comparable to existing vacuum salt production operations.

The next aspect to note is the ability of a salt market to absorb the produced salt. For perspective, in 2009, the global production of salt was 210 million tonnes/year [68] while that for vacuum salt was 60 million tonnes/year [68]. In 2017, the salt production capacities in China, USA, India, Germany, Australia and Spain were 68, 43, 26, 13, 11 and 4.3 million tonnes/year [72]. Thus, an optimal RO-ED-crystallizer system designed for a 150,000 m³/day seawater RO plant producing 1.17 million tonnes/year of salt will contribute to 0.6 % of the 2009 global salt production capacity, the equivalent of 2 % of the USA's 2017 salt production capacity, 11 % of Australia's 2017 salt production capacity or 27 % of Spain's 2017 salt

production capacity. Clearly, even one seawater RO plant outfitted with an optimized ED and crystallize system could significantly impact the local salt market. The feasibility of the concept is contingent on the location.

The next aspect to consider is the market price of salt. The price of salt varies from 10-190 \$/tonne-salt depending on purity [73], cost of production, cost of transportation etc. In the USA, the average price of rock salt, solar salt and vacuum salt is 45, 90 and 190 \$/tonne-salt [72]. From the known amounts of salt produced of each type in the USA, we can obtain a total average price of salt in the USA of 48 \$/tonne-salt. That said, there is a large variation in salt prices because of transportation costs [58]. Near a salt production facility, the prices will be close to the production costs. For reference, efficient solar salt producers produce solar salt at a cost of 5-10 \$/tonne-salt and vacuum salt at 30-50 \$/tonne-salt [58, 63]. Keeping these prices in mind, we can better analyze how the market price of salt can affect the economic feasibility of the RO-ED-crystallizer zero brine discharge concept.

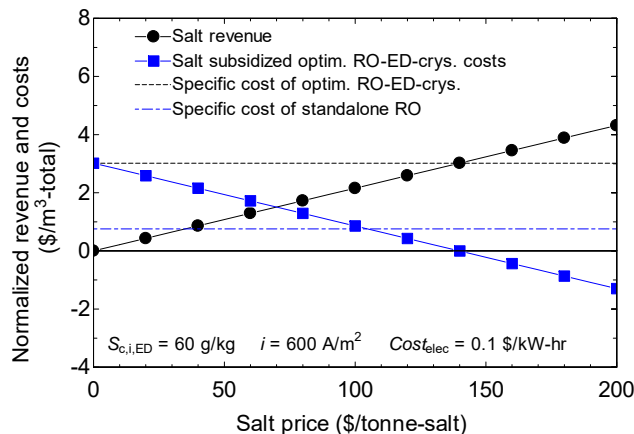


Figure 17: Specific salt revenue from salt production (8) and specific cost of an optimized RO-ED-crystallizer subsidized by specific salt revenue plotted against salt prices. The specific cost of the optimized RO-ED-crystallizer, the specific and Eq. 8 cost of a standalone RO system and a zero line are also shown. Specific costs and revenue values were obtained by normalizing costs and revenue to the total water produced (see Eq. 6 and Eq. 8)

For capturing the effect of revenue from salt production, we plotted revenue from salt production normalized to total water produced from the RO-ED-crystallizer (see Eq. 8) against the price of salt in Fig. 17. The specific cost of an RO-ED-crystallizer optimized for an electricity price of 10 US cents/kWh_e (i.e. 3.0 \$/m³) is also marked on the figure along with the specific cost of the RO-ED-crystallizer subsidized by specific salt revenue. The specific cost of a standalone 150,000 m³/day seawater RO system (i.e. 0.76 \$/m³) is also marked. For reference, the purity of the salt produced by the RO-ED-crystallizer is expected to be 99.8%.

While vacuum salt prices do go up as high as 190 \$/tonne-salt [72], practically only a few places in the world could support another 1.17 million tonnes/year of salt at those prices. For reference, in the USA only about 4 million tonnes/year of salt is sold at an average price of 190 \$/tonne-salt [72]. Furthermore, since

not all salt applications require salt of very high purity, a salt price of 30-50 \$/tonne-salt is more reasonable to assume. A salt price of 30 \$/tonne-salt translates to a specific salt revenue of 0.6 \$/m³ of water produced, subsidizing the specific cost of the RO-ED-crystallizer to 2.4 \$/m³ — a reduction of 21 %. At a salt price of 50 \$/tonne-salt, the specific salt revenue is 1.1 \$/m³ subsidizing the RO-ED-crystallizer specific cost to 1.9 \$/m³ — a reduction of 37 %. At a salt price of 104.5 \$/tonne-salt, the subsidized specific cost of a RO-ED-crystallizer is the same as that of a standalone seawater RO plant. At a salt price of 140 \$/tonne-salt, the salt revenue completely pays for the RO-ED-crystallizer. These salt prices and the resulting subsidized RO-ED-crystallizer specific costs are summarized in Table 3.

4.8. Overall techno-economic feasibility

From Section 4.6 and Section 4.7, it is quite clear that production of salt alone cannot justify the costs to retrofit many seawater RO plants with ED-crystallizers. Just a few retrofitted seawater desalination plants could easily overwhelm the salt production market and crash salt prices in a small country. In Spain, retrofitting three 150,000 m³/day seawater RO plants would almost match Spain’s existing salt production capacity. Zero brine discharge desalination through RO-ED-crystallizers will need regulatory support for general adoption. That said, the proposed RO-ED-crystallizer zero brine discharge desalination concept can be economical in select installations around the world. The design could be fully economically feasible in Saudi Arabia where existing water production costs and market prices of vacuum salt are high — 1 \$/m³ [58, 74] and 190 \$/tonne-salt [58, 75] respectively. Water production costs in Kuwait are similarly high at 0.83 \$/m³ [58, 76] with average salt prices of 100 \$/tonne-salt. Both countries have active chemical production industries requiring salt.

Overall, in select locations in the Middle East region, the proposed RO-ED-crystallizer concept could be cost competitive with standalone seawater RO systems. The recovery of minerals other than sodium chloride, such as calcium and magnesium salts, from seawater may further improve the economics of zero brine discharge desalination. This topic has potential for future research to further valorize brine. Overall, whenever regulatory pressures force the adoption of zero brine discharge technologies, the production of salt by optimized RO-ED-crystallizers can be considered as a viable pathway for the industry to meet regulations.

5. Conclusions

A detailed technical and economic analysis of the application of an RO-ED-crystallizer system for zero brine discharge desalination was conducted and an optimal configuration was determined. The key conclusions of the analysis are summarized below.

- When ED-crystallizer systems are integrated with a large seawater RO plant, all the RO brine should be split between the ED diluate and the concentrate, with no addition of seawater to the ED diluate

side (i.e., $SDR = 0$). While flowing only seawater in the ED diluate channel brine (i.e., $SDR = 1$) was beneficial when salt production was the main priority, flowing only RO brine in to the diluate channel was far more cost effective when the main priority was producing water while achieving zero brine discharge, with the switch from seawater to RO brine reducing specific costs from 27 $\$/m^3$ to 3.5 $\$/m^3$.

- The outlet salinity of the ED diluate stream strongly affected costs and must be considered carefully based on environmental regulations.
- The optimal current density of the ED system is contingent on electricity prices. At a generic electricity price of 10 US cents/ kWh_e , increasing current density from conventional operation at 300 A/m^2 to 600 A/m^2 reduced RO-ED-crystallizer specific costs by 14 % to 3.0 $\$/m^3$ but increased specific energy consumption by 26 % to 12.7 kWh_e/m^3 . In general, as long as the electricity price was less than 30 US cents/ kWh_e , increasing ED current density beyond 300 A/m^2 reduced costs.
- While hybridizing ED with HPRO did reduce costs when the priority was to produce salt in Nayar et al. [58], the addition of an HPRO stage actually increased specific costs when the priority was to produce water while achieving zero brine discharge. Thus, for zero brine discharge seawater desalination, adding an HPRO stage to a conventional seawater RO system is not necessary.
- For an electricity price of 10 US cents/ kWh_e with a ED diluate outlet salinity of 45 g/kg, the lowest cost design had an SDR of 0 and no HPRO stage, with the specific cost of the RO-ED-crystallizer (i.e., specific cost of water without accounting for salt revenue) being 3.0 $\$/m^3$ and the specific energy consumption being 12.7 kWh_e/m^3 corresponding to a Second Law efficiency of 18 %.
- The least work and actual specific energy consumption for “partial desalination” using an RO-ED-crystallizer producing salt, pure water, an ED diluate stream and a crystallizer purge stream was significantly lower than the least work and actual specific energy consumption for “complete separation” of seawater in to salt and pure water using a state-of-the-art MVC-crystallizer system.
- Production of salt from the crystallizer can subsidize the cost of RO-ED-crystallizers, but not enough to make the system economically competitive with conventional seawater RO except in select locations in the world with water scarcity where salt prices are greater than 104.5 $\$/tonne-salt$. Thus, the RO-ED-crystallizer concept may be viable in Kuwait, Saudi Arabia and other parts of the Middle-East. Regulations will be needed for the proposed RO-ED-crystallizer concept to be adopted more widely beyond these select locations. Without regulatory pressures, ED-crystallizers can only be integrated with a few seawater RO plants within a country because the total salt that could be produced from desalination plants could easily overwhelm existing markets reducing salt prices. Specific costs of

RO-ED-crystallizers outlined here are intended to inform policy makers as they deliberate regulations limiting the discharge of desalination brine to the sea.

We recommend that future research and developments efforts in the area focus on increasing the outlet brine salinity from the ED concentrate channel to limit the size of the crystallizer, piloting high current density ED systems (i.e. $> 300 \text{ A/m}^2$), and explore further valorization of brine by producing other salts in addition to sodium chloride to improve the economics of zero brine discharge desalination.

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Nomenclature

Acronyms

CapEx	capital expense, \$
Cap _{fac}	capacity factor, -
Cost _{elec}	electricity cost, \$/kWh _e
crys.	crystallizer
DCR	ED diluate to concentrate flow rate ratio, -
ED	electrodialysis
HPRO	high pressure reverse osmosis
MW	molecular weight, g/kg
OpEx	operating expense, \$
Price _{water}	water price, \$/m ³
RO	reverse osmosis
SDR	Seawater diluate ratio, -
SpCapEx	specific capital expense, \$/tonne-salt
SpCost	specific cost, \$/tonne-salt
SpOpEx	specific operating expense, \$/tonne-salt

Roman Symbols

\dot{G}	Gibbs free energy flow rate, J/s
\dot{m}	mass flow rate, kg/s
m	molality, mol/kg
\dot{N}	molar flow rate, mol/s
r_{return}	rate of return on capital, %
R	Universal gas constant, J/mol-K
S	salinity, g-salt/kg-solution

t_{life}	project life, years
T	temperature in Kelvin, K
\dot{V}	volume flow rate, m ³ /s
\dot{W}	Power, W

Greek Symbols

Δ	difference
η_{II}	Second Law efficiency
γ	mean molal activity coefficient, -
ϕ	osmotic coefficient, -
μ	chemical potential, J/mol
ν	sum of stoichiometric coefficients, -

Subscripts

crys.	crystallizer
ED	electrodialysis
f	feed
HPRO	high pressure reverse osmosis
i	inlet, index
o	outlet
p	product
pump	pump
purge	crystallizer purge stream
RO	reverse osmosis
s	salt
sw	seawater
w	water

Superscripts

0	reference state
least	thermodynamic least

Appendix A. Least work analysis

Appendix A.1. Methodology

Figure A.18 shows the RO-ED-crystallizer system with three control volumes drawn around the RO-ED, crystallizer and RO-ED-crystallizer systems. All the streams entering and leaving the systems and the work inputs to the systems have been shown.

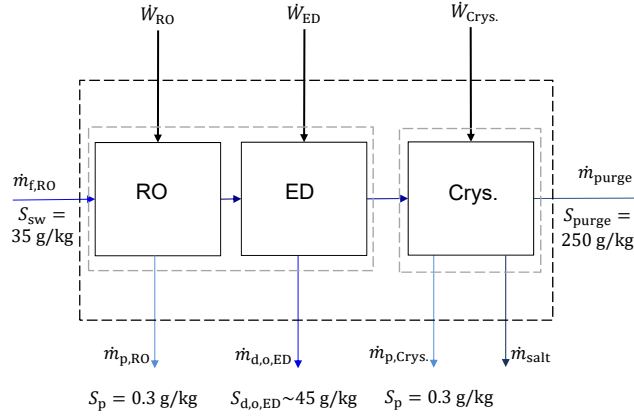


Figure A.18: Flow diagram of an RO-ED-crystallizer with control volumes drawn around the RO-ED, crystallizer and RO-ED-crystallizer systems.

A framework for evaluating the Second Law efficiency of brine concentration and crystallizer systems was presented by Chung et al. [14]. The Second Law efficiency of any system was reported by Chung et al. as:

$$\eta_{II} \equiv \frac{\text{least exergy of separation}}{\text{exergy input}} \quad (\text{A.1})$$

For a system without any heat transfer and with only work transfer in to the system, such as the one shown in Fig. A.18, the Second Law efficiency can be simplified and expressed as[14]:

$$\eta_{II} = \frac{\dot{W}_{\text{in}}^{\text{least}}}{\dot{W}_{\text{in}}} \quad (\text{A.2})$$

where $\dot{W}_{\text{in}}^{\text{least}}$ is the thermodynamic least work needed to be transferred in to the system to go from an initial state to a desired final state (i.e., no entropy is generated in the control volume) while \dot{W}_{in} is the actual work transferred to go from in between the same states. The thermodynamic least work for a given control volume is purely a function of the states of the streams entering and leaving the control volume. Thiel et al. [54] had calculated that for an open system in which streams are entering and leaving at the same temperature as the environment, the thermodynamic least work can be expressed as an algebraic sum of the Gibbs free

energies of the streams leaving and entering:

$$\dot{W}_{\text{in}}^{\text{least}} = \sum_o \dot{G}_o - \sum_i \dot{G}_i \quad (\text{A.3})$$

Just like in Chung et al. [14], for calculating least work, we assume that seawater is aqueous sodium chloride. Thus, the Gibbs free energy of any stream can be expressed as a molar sum of the chemical potential of the salt and water components [77]:

$$\dot{G}_i = \dot{N}_{s,i} \mu_{s,i} + \dot{N}_{w,i} \mu_{w,i} \quad (\text{A.4})$$

Thus, the least work for a given control volume is:

$$\begin{aligned} \dot{W}_{\text{in}}^{\text{least}} = \sum_o \left(\dot{N}_{s,o} \mu_{s,o} + \dot{N}_{w,o} \mu_{w,o} \right) - \\ \sum_i \left(\dot{N}_{s,i} \mu_{s,i} + \dot{N}_{w,i} \mu_{w,i} \right) \end{aligned} \quad (\text{A.5})$$

where μ_s and μ_w can be calculated from McGovern et al. [78] as:

$$\mu_s = \mu_s^0 + RT \ln(\gamma m) \quad (\text{A.6})$$

$$\mu_w = \mu_w^0 + RT \phi \text{MW}_w \nu m \quad (\text{A.7})$$

where μ_s^0 is the chemical potential of salt in the reference state, R is the universal gas constant, T is temperature in K (here, 298.15 K), γ is the molal activity coefficient, m is the concentration of the salt in the stream in molality, μ_w^0 is the chemical potential of water in the reference state, ϕ is the osmotic coefficient, MW_w is the molecular weight of pure water (18.02 g/mol) and ν is the number of moles ions in the salt (here, 2). The values for γ and ϕ were obtained from Robinson and Stokes [79].

Applying Eq. A.5 to the three control volumes in Fig. A.18 we have the least work for the RO-ED, crystallizer and RO-ED-crystallizer systems:

$$\begin{aligned} \dot{W}_{\text{RO-ED}}^{\text{least}} = & \left(\dot{N}_{s,p,\text{RO}} \mu_{s,p,\text{RO}} + \dot{N}_{w,p,\text{RO}} \mu_{w,p,\text{RO}} \right) + \\ & \left(\dot{N}_{s,d,o,\text{ED}} \mu_{s,d,o,\text{ED}} + \dot{N}_{w,d,o,\text{ED}} \mu_{w,d,o,\text{ED}} \right) + \\ & \left(\dot{N}_{s,c,o,\text{ED}} \mu_{s,c,o,\text{ED}} + \dot{N}_{w,c,o,\text{ED}} \mu_{w,c,o,\text{ED}} \right) - \\ & \left(\dot{N}_{s,f,\text{RO}} \mu_{s,f,\text{RO}} + \dot{N}_{w,f,\text{RO}} \mu_{w,f,\text{RO}} \right) \end{aligned} \quad (\text{A.8})$$

$$\begin{aligned}
\dot{W}_{\text{crys.}}^{\text{least}} = & \left(\dot{N}_{\text{s,p,crys.}} \mu_{\text{s,p,crys.}} + \dot{N}_{\text{w,p,crys.}} \mu_{\text{w,p,crys.}} \right) + \\
& \left(\dot{N}_{\text{s,purge}} \mu_{\text{s,purge}} + \dot{N}_{\text{w,purge}} \mu_{\text{w,purge}} \right) + \\
& \left(\dot{N}_{\text{s,salt}} \mu_{\text{s,salt}} \right) - \\
& \left(\dot{N}_{\text{s,c,o,ED}} \mu_{\text{s,c,o,ED}} + \dot{N}_{\text{w,c,o,ED}} \mu_{\text{w,c,o,ED}} \right)
\end{aligned} \tag{A.9}$$

$$\dot{W}_{\text{RO-ED-crys.}}^{\text{least}} = \dot{W}_{\text{RO-ED}}^{\text{least}} + \dot{W}_{\text{crys.}}^{\text{least}} \tag{A.10}$$

where, $\mu_{\text{s,salt}}$ was numerically equivalent to the chemical potential of salt in a saturated solution of sodium chloride [14].

To verify the accuracy of the approach described above for calculating least work, the same framework was applied to calculating the least work for conventional seawater desalination and the results were verified against values reported in the literature[8, 10, 80].

The Second Law efficiencies for the RO-ED, crystallizer and RO-ED-crystallizer systems were obtained by applying Eq. A.1 to the three systems:

$$\eta_{II, \text{RO-ED}} = \frac{\dot{W}_{\text{RO-ED}}^{\text{least}}}{\dot{W}_{\text{RO}} + \dot{W}_{\text{ED}}} \tag{A.11}$$

$$\eta_{II, \text{crys.}} = \frac{\dot{W}_{\text{crys.}}^{\text{least}}}{\dot{W}_{\text{crys.}}} \tag{A.12}$$

$$\eta_{II, \text{RO-ED-crys.}} = \frac{\dot{W}_{\text{RO-ED-crys.}}^{\text{least}}}{\dot{W}_{\text{RO}} + \dot{W}_{\text{ED}} + \dot{W}_{\text{crys.}}} \tag{A.13}$$

Appendix A.2. Results

Figure A.19 shows the least work for the RO-ED, crystallizer and RO-ED-crystallizer systems for the optimized configuration with SDR = 0, 42 % RO RR and an ED current density of 600 A/m² (case 3 in Table 2). The RO-ED system had a least work of 1.4 kWh_e/m³ while the crystallizer had a least work of 0.9 kWh_e/m³ with the least work for the complete RO-ED-crystallizer system being 2.3 kWh_e/m³.

Least work for partial desalination was significantly less than complete desalination

If the values for least work are normalized per mass flow rate of seawater feed instead of the volume flow rate of product water, the least work for the RO-ED, crystallizer and RO-ED-crystallizer systems were 2.3, 1.5 and 3.8 kJ/kg-feed respectively. In comparison, the least work reported by Chung et al. [14] for brine concentration (concentrating seawater from 35 to 264 g/kg) was 6.9 kJ/kg-feed and that for crystallization

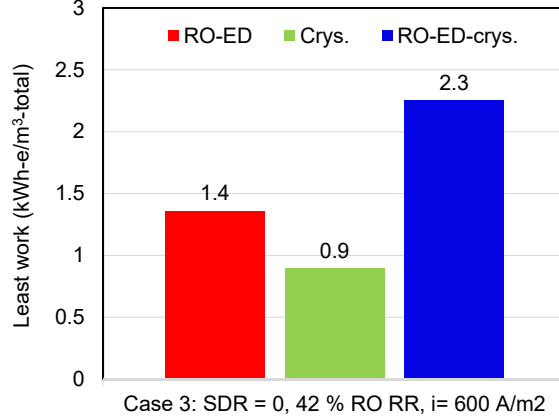


Figure A.19: Least work for the RO-ED, crystallizer and RO-ED-crystallizer systems for a configuration with SDR = 0, 42 % RO recovery and ED current density of 600 A/m² (case 3 in Table 2).

(concentrating from 264 g/kg salinity to complete separation into salt and water) was 3.8 kJ/kg-feed with the least work for the complete process (from 35 g/kg to complete separation) being 10.8 kJ/kg-feed. Thus, the least work for the RO-ED-crystallizer configuration with partial desalination was 2.8 times lower than the least work for complete separation of seawater in to salt and pure water.

The results for the Second Law efficiencies of the three systems were reported in Fig. 16.

Appendix B. Cost model for high pressure reverse osmosis

Nayar et al. [58] had reported a detailed cost model for a 305 m³/day HPRO system. The cost model was based on the cost of RO from DesalData’s cost estimator [81] which was built on a large sample of actual seawater RO plant data. Nayar et al. had used a breakdown of seawater RO capital costs across the constituent components from DesalData to isolate the components whose costs are affected by pressure. These consisted of piping, pumps, membranes, pressure vessels and energy recovery devices (ERDs). The cost of these components when the operating pressure is increased from 60 bar to 120 bar was calculated by Nayar et al. using both quotes from parts suppliers and by using standard engineering equations to calculate the required thickness of pipes and pressure vessels. Nayar et al. [58] had reported that at 120 bar, the piping, pumps, membranes, pressure vessels and ERDs costed 1.24, 1.67, 3, 1.67 and 1.67 times the cost at 60 bar.

For the analysis presented in this paper, the same HPRO model used by Nayar et al. [58] was used, but the capital cost numbers were scaled for the much larger HPRO capacity of 100,000-150,000 m³/day.

First, we obtained the capital cost of a 150,000 m³/day conventional seawater RO plant and the cost breakdown across components from DesalData [81]. Table B.4 shows the input data used for the calculator. Figure B.20 shows the output: a breakdown of the total capital costs of a seawater RO plant across all its

Table B.4: Input variables used on DesalData [81] to obtain capital costs for a conventional seawater RO plant

Plant feature	Data
Capacity	150,000 m ³ /day
Seawater salinity	30,000 mg/L
Seawater min. temp.	15 °C
Seawater max. temp.	24 °C
Pretreatment	Standard
Second pass	0%
Remineralization	No
Intake/Outfall	Typical
Permitting	Typical
Country	Any

Table B.5: Break down of capital cost of RO and HPRO per m³/day production capacity for a 150,000 m³/day plant. RO capital costs obtained from Desaldata [81].

CapEx contributor	RO CapEx (\$-day/m ³)	HPRO-RO CapEx ratio	HPRO CapEx (\$-day/m ³)
Equipment and materials	\$ 247	1	\$247
Civil costs	\$ 241	1	\$241
Installation services	\$ 109	1	\$109
Intake / Outfall	\$ 102	0	\$0
Pretreatment	\$ 96	0	\$0
Design costs	\$ 78	1	\$78
Legal and professional	\$ 16	1	\$16
Piping, high-grade alloy	\$ 147	1.24	\$182
Pumps	\$ 97	1.67	\$161
Membranes	\$ 59	3	\$178
Pressure vessels	\$ 17	1.67	\$28
Energy recovery devices	\$ 11	1.67	\$18
Total	\$ 1,219		\$1,258

constituent components. The five terms affected by pressure: piping, pumps, membranes, pressure vessels and energy recovery devices, together contributed only 27% to the overall capital costs for a seawater RO plant. Table B.5 shows the specific capital cost of each component of a 150,000 m³/day seawater RO plant, a conversion factor to convert the component cost from RO to HPRO and the final estimated cost of each component of a HPRO stage of the same size. The total specific capital cost of a 150,000 m³/day seawater RO plant was 1219 \$-day/m³ RO product water. The same conversion factors for HPRO reported by Nayar et al. [58] were used to calculate the specific capital cost of HPRO. The specific capital cost of a 150,000 m³/day HPRO plant was 1258 \$-day/m³ HPRO product water — 1.03 times the specific capital cost of conventional seawater RO:

$$\text{SpCapEx}_{\text{HPRO,p,day}} = 1.03 \times \text{SpCapEx}_{\text{RO,p,day}} \quad (\text{B.1})$$

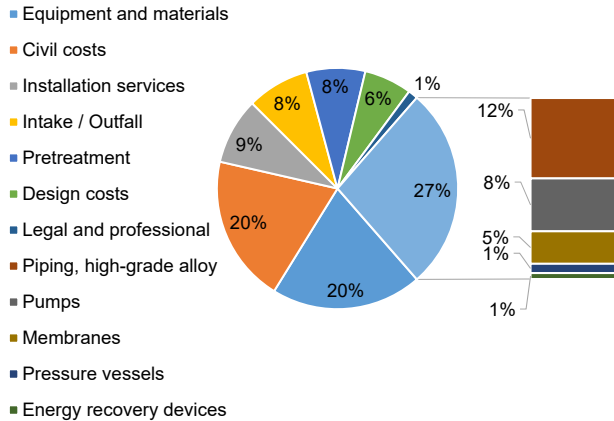


Figure B.20: Breakdown of capital costs in an RO plant with the data sourced from Desaldata [81]. The components affected by pressure account for 27 % of the capital costs.

For comparison, Nayar et al. [58] had reported that HPRO cost 1.09 times the cost of conventional seawater RO for a capacity of 305 $\$/\text{day}/\text{m}^3$. Other aspects of the HPRO model reported by Nayar et al. were directly applicable to the analysis presented in this paper.

Appendix C. Discussion on nanofiltration

Nanofiltration (NF) can selectively remove divalent ions and has been considered previously in the literature as a pre-treatment method for conventional seawater RO to reduce divalent scale formation on the membranes [82, 83]. For the benefit of readers, we evaluated the approximate costs of NF pre-treatment.

For the analysis reported in this paper, the NF cost and process model reported previously by Nayar et al. [58] was adapted to a configuration with $\text{SDR} = 0$. The NF cost and process model was informed by industrial data [61, 84], projections from Dow Chemical’s ROSA program [85] for the NF-270 membrane and recommendations from an antiscalant company [71].

NF cost and energy consumption is contingent on the configuration of the NF system, which ultimately depends on what purpose an NF system is deployed for. NF may be used to improve the purity of the salt produced, reduce maintenance costs in the crystallizer, increase HPRO membrane life if an HPRO system is deployed, enable the recovery of calcium and magnesium salts etc. For the benefit of readers, we chose a generic configuration where NF was used to treat a 100 % of the RO feed. This configuration we believe provided an approximate upper bound for the cost of NF pre-treatment.

NF system costs are also heavily influenced by the recovery ratio at which the NF system is operated — higher the recovery, lower the feed flow rate to the NF system and lower the costs. Data in the literature on the operation of a seawater NF pilot plant [84] had reported an NF recovery of 70 %. For seawater feed, Nayar et al. [58] had verified that with the use of the appropriate antiscalants[71], an NF system using Dow’s NF-270 membrane could be operated at a recovery of 70 %.

In an NF-RO-ED-crys. configuration, the NF specific cost and energy consumption values were 0.94 $\$/\text{m}^3$ and 2.1 kWh_e/m^3 respectively. For comparison, the RO system had a specific cost and energy consumption of 0.69 $\$/\text{m}^3$ and 1.8 kWh_e/m^3 respectively. Thus, when NF is used to treat a 100 % of the RO feed, the NF specific costs and energy consumption is actually higher than that of the RO system.

In an NF-RO-HPRO-ED-crys. configuration, the NF specific cost and energy consumption values were 0.53 $\$/\text{m}^3$ and 1.2 kWh_e/m^3 respectively. For comparison, the RO-HPRO systems had a specific cost and energy consumption of 0.76 $\$/\text{m}^3$ and 2.6 kWh_e/m^3 respectively. Here, NF specific cost and energy consumption was lower than the RO-HPRO system. This was because the overall recovery of the RO-HPRO system was higher than that of standalone RO (71 % vs. 42 %) leading to a lower RO feed flow rate and a much smaller NF system.

It can be seen that NF costs can vary depending on the configuration. With the appropriate NF membranes and system design, NF could be used in between the RO and HPRO systems, or to treat the diluate leaving the ED system. Since the flow rates in these cases are lower than the cases we discussed, the costs in other configurations are expected to be lower. We would like to reiterate here that the NF specific cost and energy consumption values discussed here are estimates from a model. Detailed laboratory scale NF experiments should be conducted to ascertain NF performance, potential for scaling, and to properly weigh the benefits of NF against the cost of NF.