Limits of High Recovery Inland Desalination: Closed-Circuit Reverse Osmosis – a Viable Option?

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DOI: 10.1002/cite.202100042

Cost-efficient operation of inland brackish water reverse osmosis (BWRO) demands a high recovery. As recovery of BWRO is often limited to scaling, antiscalants (AS) are applied, whose environmental impact is disputed. In this paper, different systems (conventional single- and two-stage plug flow RO (PFRO) and closed-circuit RO (CCRO)) were simulated in various configurations (AS dosing, ion exchange (IEX) pretreatment, elements per vessel) to determine the recovery limiting factor for a hard feed. The novel proposed IEX-CCRO reached the highest recovery without AS dosing. PFRO configurations had lower recoveries, mainly due to hydraulic limitations. Utilizing RO brine reduced both the water demand and salts necessary for IEX regeneration.

Keywords: Closed-circuit reverse osmosis, Process simulation, Resource recovery, Scaling

Received: April 25, 2021; *accepted:* June 15, 2021

1 Introduction

Reverse osmosis (RO) is increasingly applied for inland brackish water (BW) desalination to supply potable and treated water for agriculture and industrial purposes [1]. Nevertheless, brine management is challenging [2]. Direct discharge to the environment (e.g., aquifer, river) is limited by stringent restrictions while indirect discharge is usually not economically feasible [3]. Further on, the quantity of source water might be limited, e.g., by the permission for groundwater abstraction. Accordingly, a high recovery (ϕ), which is the ratio of permeate volume rate (Q_P) to feed flow volume rate (Q_F), is demanded to reduce the brine volume, and thus, the costs for inland BWRO. Moreover, the system size (storage tanks, raw-feed pumps, chemical dosing, etc.) is determined by feed and concentrate flow rates and thus increasing the recovery potentially decreases both, investment and operating costs [4]. Last but not least low recoveries are detrimental for scarce water sources [5].

Typically, BWRO is operated with spiral wound elements (SWE) arranged in pressure vessels (PV) at a pressure of 10–15 bar, reaching recoveries of 75–80 % [6, 7]. Since the recovery of single-stage (PV with maximum 8 SWE in series) operation is generally restricted to 50 % [3], a typically BWRO is operated with two stages as a staged array [1]. For groundwater treatment an array configuration of 2:1, i.e., the first stage has twice as many PV as the subsequent stage of which the feed is the concentrate of the first stage, is commonly used [1, 3]. Customary 6-m PV equipped with 6 SWE are implemented.

The recovery of BWRO is most often limited by scaling [2, 5–7] which occurs on the membrane surface or onto feed spacer fibers by precipitation of supersaturated sparingly soluble salts at concentrations higher than the solubility limit [5]. The degree of supersaturation can be determined with the saturation index (*SI*), which is the logarithmic fraction of the ion activity product to the solubility product of the respective ions and salt [8, 9]. In thermodynamic equilibrium ($SI = 0$), the fraction of the ion activity product and the solubility product is in unity. When the ion activity product exceeds the solubility product ($SI > 0$), precipitation is thermodynamically attainable [10] to regain equilibrium. For calcium carbonate, the Langelier saturation index (*LSI*), is commonly applied to assess the saturation [5, 10]. Besides thermodynamic conditions,

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kinetics, e.g., expressed by nucleation induction times, are decisive to evaluate the possibility and the relevance of scaling in membrane processes [8, 10]. The highest probability for the occurrence of scaling is found at the highest concentration of rejected ions and thus in the concentrate at the outlet of the rear element of the last stage (also called brine or retentate) [7, 8]. This concentration depends on the recovery and membrane salt retention. The concentration factor (*CF*), which is the ratio of solute concentration in the concentrate (c_C) to its concentration in the feed (c_F) can be expressed by Eq. (1) being a reliable approximation for a salt rejection above 90 % [3]:

$$CF = \frac{c_c}{c_F} = \frac{1}{1-\phi} \tag{1}$$

For a recovery range of 75–90 %, the solute concentration from feed to the brine increases by *CF* = 4–10. Such concentration increase may result in positive *SI* of certain salts, and thus, induce scaling [5]. Scaling causes, among other things, reduced permeate flux (and quality), membrane deterioration and hence higher operating costs [10]. Common salts inducing scaling are calcium carbonate (e.g., calcite and aragonite), calcium sulfate, calcium phosphate, calcium fluoride, barium sulfate, strontium sulfate and (amorphous) silica forms [5, 8, 10, 11].

Anitscalants (AS) are chemicals dosed to the feed upstream of the membrane module to impede scaling [2, 8], by prolonging the induction time and/or decelerating the crystal growth and thus enable to extend the saturation limits of sparingly soluble salts [10–13]. AS are distinguished according to their main functional group in phosphates, phosphonates and polycarboxylates [8, 10]. AS dosing is a customary procedure in practical operation [3, 10]. However, there are growing concerns regarding the direct discharge of AS-containing concentrates [13]. Moreover, AS are not sufficient for each scaling forming salt (e.g., calcium phosphate) and are usually designed to target certain scaling minerals, thus depending on the feed composition multiple AS might be necessary [10]. Besides, AS substances are expensive [14], and can induce membrane fouling [11]. Inorganic acids may occasionally be dosed to prevent scaling, particularly for calcium carbonate and phosphate scaling [3, 10], solely, and in combination with AS [11].

Another approach to reduce scaling in RO plants is the selective removal of scale-forming anions (e.g., CO_3^{2-}, PO_4^{3-}, SO_4^{2-}) and/or cations (e.g., Ca^{2+}, Mg^{2+}) from upstream using ion-exchangers (IEX) [10, 14, 15]. IEX are able to exchange anions and cations in an electrolyte solution with a charge equivalent amount of ions [16]. As an example, a strong acid cation (SAC)-IEX in the Na^+-form is used to soften water, thus exchanging the total hardness (TH), i.e., Ca^{2+} and Mg^{2+}, with a charge equivalent amount of Na^+ [5]. The SAC-IEX resin has only a certain capacity and has to be regenerated frequently, e.g., with a high concentrated (3-14 wt.-%) NaCl solution [5]. IEX as a pretreatment step in desalination technologies to prevent scaling is not a novel approach. In the 1970s and 1980s, Vermeulen and colleagues worked on hybrid IEX-desalination processes to reduce sulfate-, carbonate- and hydroxide scaling and prevent acid corrosion [15]. Besides, the suitable application of the hybrid IEX-desalination (RO and evaporation), inter alia, for seawater desalination (evaporation) to reduce sulfate scaling and the RO treatment of agriculture drain, they showed the feasibility of a self-sustaining (after an initial regeneration-salt input to the system) process by using the brine (of both evaporation and RO) for the regeneration of the IEX [15]. More recently, Vanoppen et al. [14] demonstrated the feasibility of a hybrid ion exchange RO process for the treatment of surface water. The study showed that the pretreatment step with a SAC-IEX increases the recovery of the RO from 75 to 85 %, without AS [14]. In addition, the RO concentrate could be employed to regenerate the exhausted IEX [14]. Although complete regeneration of IEX using RO concentrate may not be reached, the amount of added NaCl could be reduced significantly [14]. Softening via precipitation is another common approach to mitigate $CaCO_3$ scaling; but is not further considered here and can be found, e.g., in Stetter [16].

Time-varying RO processes, like batch and semi-batch RO and pulse-flow RO, have been reported to have high resistance toward fouling, and in particular, scaling [17–20]. Closed-circuit RO (CCRO) is a semi-batch RO process introduced by Efraty et al. [21] and is commercially distributed by Desalitech (DuPont). A typical scheme of a semi-batch RO process is shown in Fig. 1.

Semi-batch operation comprises two modes (not considering the transition in between), closed-circuit (CC) operation and flushing [20]. In CC-mode, the feed flow rate is equal to the permeate flow while no brine is produced (Q_B = 0), and the concentrate is recirculated and mixed with the feed ($Q_F + Q_C$). The solute concentration increases within CC-mode with each pass, depending on the CC recovery (ϕ_{CC}), cf. Eq. (2).

$$\phi_{CC} = \frac{Q_P}{Q_F + Q_C} = \frac{Q_P}{Q_{F,i}} \tag{2}$$

The high-pressure pump (HP) increases subsequently the hydraulic pressure concurring to increasing osmotic pressure (due to permeate production), while the circulation pump (CP) supplies sufficient and adjustable crossflow velocity [20]. Moreover, the CP compensates for the pressure loss within the system. When a specific solute concentration is reached, the flushing valve opens, and the brine (Q_B) is discharged. Thereafter, the system volume is replenished with feed, and a new cycle starts [1]. Stover and Efraty [20] reported for BW-CCRO being in CC-mode 85–90 % of the time and 10–15 % being flushed. The plant recovery can then be determined by the time-weighted permeate production in both modes. In contrast to conventional RO, recovery in CCRO depends on the cycle length rather than

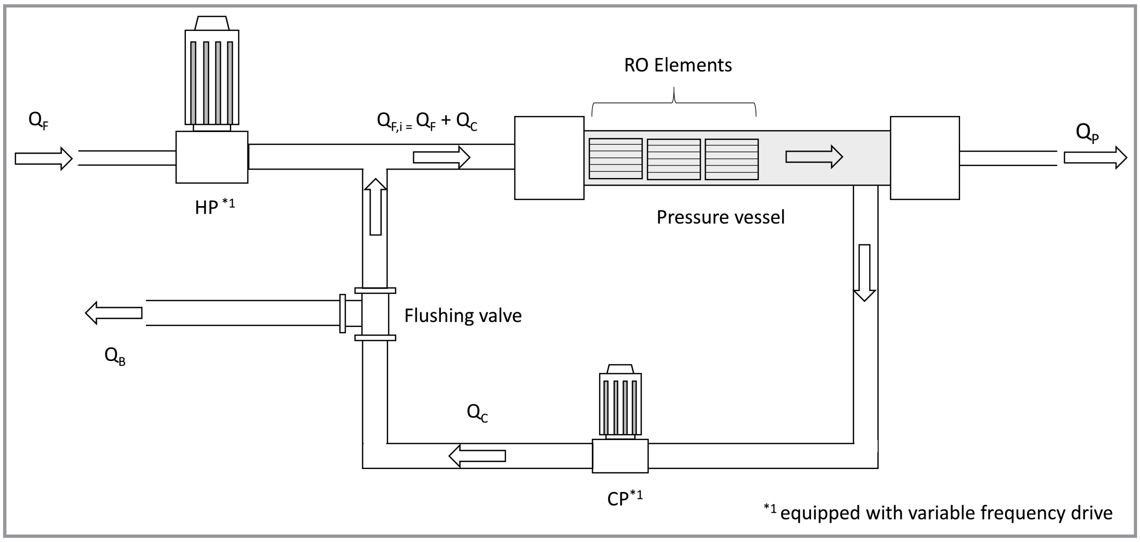

Figure 1. Scheme of a typical semi-batch system.

elements and/or stages number [20]. Consequently, CCRO is operated with fewer elements (3–4 in series) and without the need for multiple stages [20].

The primary motivation for the development of CCRO was saving energy in the desalination process [1, 21, 22]. Moreover, it is particularly suitable for inland BWRO due to its compact design, presumed resistance toward scaling and fouling, and high flexibility regarding feed water composition [20]. Inherent concentrate recirculation keeps most of the hydraulic energy in the system without the need for energy recovery devices, and high recoveries are attainable within one stage [20]. Therefore, CCRO has, compared to other high-recovery systems, such as multistage systems, high practicability and thus might be a more cost-efficient solution for BWRO [22]. The resistance toward scaling may be related to relatively short cycle times, lower than the nucleation induction time of sparingly soluble salts [17]. Although, classical RO (referred to in this work as plug flow RO (PFRO)) has relatively low concentrate detention times, Dhakal et al. [12] estimated for a typical BWRO approximately one minute, the composition of the stagnant layer close to the membrane might only be interrupted by cleaning intervals, in a time frame of about one week [17] and thus is considerably higher than in CCRO. The concept of undershooting the induction nucleation time to reduce scaling can be also exploited with PFRO by applying periodically flow reversal [23]. However, it should be noted that the concept of a nucleation induction time is disputed. For instance, Mitrouli et al. [24] did not find evidence for an induction time in practical experiments with slightly supersaturated brackish water.

Another argument for lower proneness towards scaling (and fouling) of CCRO is the possibility to adjust high crossflow velocities independent of the feed and permeate flow enabled by the CP. A higher crossflow velocity reduces concentration polarization, prevents deposition and beyond that allows increased (hydraulic) flexibility in compliance with membrane specifications [20].

2 Objectives and Outline of the Study

This study's main objective was to promote the efficiency of inland BWRO (common PFRO and emerging CCRO) by identifying limiting factors of the recovery, investigating optimizing potential and to explore possibilities to avoid AS. Different systems (single- and two-stage PFRO, CCRO) and the impact of altering configurations (e.g., PV length), with and without combination of IEX as pretreatment and AS dosing, were systematically studied by process simulation with fixed boundary conditions. Subsequently, a novel hybrid IEX-CCRO system has been introduced. Moreover, the potential of waste (brine) streams reuse was investigated to decrease disposal volume and chemical additive demand by facilitating synergetic effects of hybrid processes.

3 Material and Methods

3.1 Simulation Software and Water Chemistry Calculations

IEX, PFRO and CCRO were simulated with the design software LewaPlus (Lanxess). Due to current events Lanxess will terminate the support for CCRO dimensioning. A similar software tool (Wave) for CCRO dimensioning was released in early 2021 by DuPont. PhreeqC was used for *SI* calculations, and for mixing of solutions. It is an equilibrium-based program developed for water-chemistry calculations. Detailed information can be found in Parkhurst and Appelo [9].

3.2 BWRO Systems

Three BWRO systems were considered, single-stage PFRO, two-stage PFRO and CCRO. Although there are examples for three-stage inland BWRO, systems with more than two stages were not considered to avoid high complexity and associated investment costs to ensure transferability to practical applications. The configuration was varied for each system by altering PV length and number of loaded elements, dosing of 2 ppm AS, and/or IEX as pretreatment (hybrid: IEX-PFRO and IEX-CCRO).

3.3 Feed Water

Duisburg tap water (service area 1) of 2019 [25] was chosen as feed water due to its high hardness, sulfate and silicate content, and thus a high tendency for scaling (carbonate-, sulfate- and silicate-scaling). The tap water's water chemistry essentially matches that of the raw feed water (predominantly groundwater [25]) treated in the waterworks and was assumed to be representative groundwater with high transferability. Tab. 1 represents a brief summary of the input water composition. The detailed water composition can be found in [25].

Table 1. Composition and characteristics for Duisburg tap-water (values rounded) [25].

Parameter	Value
Temperature [°C]	13.9
pH [–]	7.23
Hydrogen carbonate [$mg\,L^{-1}$]	267
Calcium [$mg\,L^{-1}$]	102
Magnesium [$mg\,L^{-1}$]	11
Sodium [$mg\,L^{-1}$]	25
Sulfate [$mg\,L^{-1}$]	75
Silicon dioxide [$mg\,L^{-1}$]	9

Note that no mechanical pretreatment step was considered, and for the following calculations, particle-free water was assumed.

3.4 System Recovery

The recovery was calculated for each system considering the fixed permeate flow rate Q_P of 50 m^3h^{-1} (except for the case of CCRO with AS, where excess permeate was produced for applying an extended flushing, cf. Sect. 3.5, 4.2) with reference to the amount of raw water, which was fed to the system ($Q_{F,raw}$).

$$\phi_{System} = \frac{Q_P}{Q_{F,raw}} \tag{3}$$

For RO configurations without IEX as pretreatment, $Q_{F,raw}$ equals the RO feed ($Q_{F,RO}$) and thus the system recovery (ϕ_{System}) equals the RO recovery (ϕ_{RO}). For the hybrid IEX systems the additional water demand due to the IEX regeneration ($Q_{WW,IEX}$) was considered with:

$$Q_{F,raw} = Q_{F,RO} + Q_{WW,IEX} \tag{4}$$

3.5 IEX Operation and Regeneration Strategies

For the simulation of the IEX, a SAC-IEX with an S1567 resin (Lanxess) was chosen. Each IEX unit consists of two vessels, one in operation, one in regeneration or shut down. In general, units were dimensioned for an operation time of 10 h with subsequent regeneration of ~2–3 h, concurring with necessary regeneration times. The dimensions (e.g., amount of resin) of an IEX unit depend on the required softened water flow rate Q_{IEX}, and the feed water and softened water quality.

Each regeneration consisted of backwashing (Q_{BW}) with 4 bed volumes (BV), reverse exchange (Q_{RE}) with 2.15 BV and slow and fast rinsing (Q_{Rinse}), each with 2 BV. The sum of the three regeneration flows determines $Q_{WW,IEX}$ (cf. Fig. 2). Q_{RE} has a NaCl content of ~8 wt.-%, and the demand for NaCl is 180 $g_{NaCl}L_{resin}^{-1}$. For the reverse exchange, the influence of other monovalent cations, e.g., potassium, was not considered. These set parameters for the regeneration are based on both the recommended ranges of LewaPlus and the literature (e.g. [5]) and were applied for every simulation unless described differently.

Three different regeneration strategies (conventional, partial, and complete substitution) depending on the water source for the regeneration process were simulated. For the conventional regeneration process backwashing was simulated with raw feed, whereas for reverse exchange and rinsing, softened water was used. Partial substitution means that RO concentrate was used to substitute the volume of reverse exchange solution. In contrast, complete substitution means that RO concentrate was employed to substitute all regeneration flows (i.e., backwashing, reverse exchange, rinsing). Substitution with RO concentrate does not refer to replacing the dosed salt, but to the substitution of the respective liquid fraction. Strategies of supplementing regeneration agents (here NaCl) are discussed in Sect. 4.3.

Q_{IEX} varies with the chosen regeneration strategy. For conventional regeneration (cf. Fig. 2) it applies:

$$Q_{IEX} = Q_{F,RO} + Q_{Rinse} + Q_{RE} = \frac{50\ m^3/h}{\phi_{RO}} + Q_{Rinse} + Q_{RE} \tag{5}$$

Accordingly, IEX size depends on RO recovery and can thus only be specified once the recovery has been determined. For partial and complete substitution, the IEX size

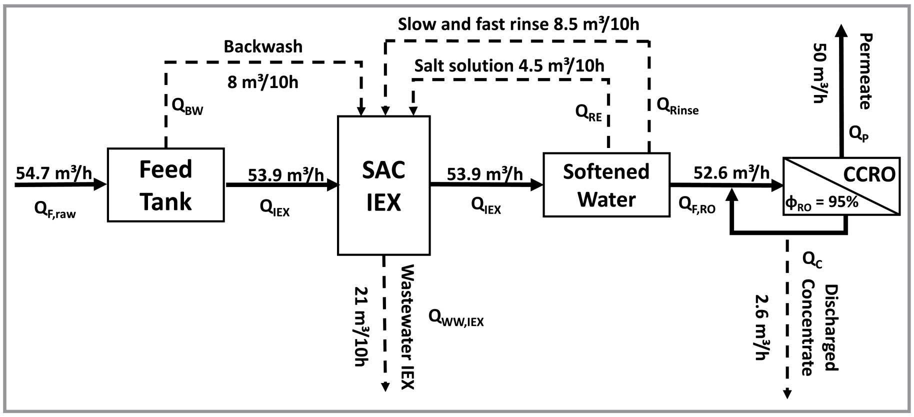

Figure 2. Schematic representation for an upper RO recovery hybrid IEX-CCRO system with conventional IEX regeneration (for extended flushing the softened water for rinsing is used, but not depicted here).

decreases compared to conventional regeneration because less water is needed to be softened. For partial substitution, the reverse exchange flow Q_{RE} is ceased, while in case of complete substitution, both Q_{RE} and Q_{Rinse} are omitted. The substitution of Q_{BW} with RO concentrate in case of complete substitution has no further influence on IEX size because otherwise (conventional and partial substitution) untreated raw feed water is used for backwashing. However, the substitution reduces $Q_{F,raw}$ and thus increases ϕ_{System}.

3.6 Operation Parameters for Maximum RO Recovery

PFRO and CCRO configurations were simulated employing 8-inch RO B400 FR ($\approx 37\,m^2$, 99.5 % salt rejection) membranes. In the case of the PFRO configurations, no booster pumps, permeate throttling or concentrate recirculation were considered for hydraulic balancing.

The recoveries for all RO systems and configurations were calculated and compared for a fixed Q_P of $50\,m^3h^{-1}$. Maximal achievable recoveries were for the given feed limited either hydraulically or by scaling. Hydraulic limitations are given by specific module or system requirements, i.e., maximum feed flow per vessel ($Q_{F,max} = 15\,m^3h^{-1}$), minimum concentrate flow per vessel ($Q_{C,min} = 3.6\,m^3h^{-1}$, silt density index $SDI_{Feed} < 5$), maximum element recovery (20 %), and maximum average permeate flux ($26\,L\,m^{-2}h^{-1}$). The relatively high concentration flow rate was designed to minimize concentration polarization. Moreover, the pressure was capped to a maximum of 20 bar. All configurations were optimized to reach the highest possible average permeate flux (in compliance with the above-mentioned limitations) by altering PV length and number of loaded elements. The scaling limitation was considered by water-chemistry calculations either by setting maximum $SI = 0$ for the operation without AS dosing, while in case of AS dosing the maximum saturation, e.g., for $CaCO_3$ was adjusted to $SI = 2.15$, which is in between the commonly reported range of 1.8–2.5 [11].

Since CCRO is suspected to be less prone toward scaling, an upper RO recovery was calculated. The upper recovery considers the nucleation induction time of the specific sparingly soluble salt and allows for temporary supersaturation of the solution during circulation. However, we defined that the respective nucleation induction time must be higher than the time span between two extended flushing procedures (which is explained later) since we addressed the issue of salt retention due to non-ideal flushing, e.g., [26, 27]. The nucleation induction time for $CaCO_3$ was calculated according to He et al. [28], and for SiO_2 according to the calculations of Warsinger et al. [17] as well as data based on the experiments of Kempter et al. [29]. In the case of $CaCO_3$, the *SI* was calculated to determine the induction time. For CCRO with AS dosing, the described induction time approach is not applicable due to the retarding effect of AS. Instead, the upper recovery for CCRO was calculated according to induction times in the presence of AS found in [12]. Moreover, to avoid inadmissible salt accumulation in consecutive cycles of CCRO an extended flushing after a certain number of cycles was assumed to be necessary in addition to the conventional flushing after each cycle. Conventional flushing is done to displace the concentrate volume after finishing a cycle by applying an equal volume of feed whereas in extended flushing a larger volume is applied. It is intended to restore initial conditions and thus prevent salt accumulation, which would cause higher average osmotic pressure and scaling.

4 Results and Discussion

Since both hybrid systems, IEX-PFRO and IEX-CCRO configurations were found to be not limited by $CaCO_3$ scaling (cf. Sect. 4.1 and 4.2), co-flow softening was identified to be sufficient (TH requires only three log-stages elimination with regard to the equivalent concentration). Co-flow is typically applied for softening and relatively simple to design and to operate (e.g., easy backwashing). A more sophisticated softening (e.g., counterflow or fluidized bed) was thus not necessary and co-flow was sufficient for both the service and the regeneration process.

It should be noted that the osmotic pressure in the softened water increased compared to the raw feed water due to the exchange of 1 mol TH with 2 mol sodium. Accordingly, hybrid IEX configurations had higher initial osmotic pressure than those with raw feed (0.34 bar vs. 0.26 bar). This could be considered a small deviation, mainly because the osmotic pressure in BWRO is, in contrast to SWRO [5], not a major concern. Nevertheless, at high recoveries, higher osmotic pressure could be decisive since the upper recovery (95 %) of the IEX-CCRO was set by the maximum pressure limitation (20 bar). In comparison, the untreated feed could (theoretically) reach approximately factor 1.3 higher *CF* and thus a higher recovery (96–97 %) at the same set net pressure and comply with the set maximum pressure limitation.

Tab. 2 summarizes the results for maximum system recovery, limitations for different systems and configurations, average fluxes, and number of elements.

4.1 Performance of PFRO Systems

RO recovery in single-stage PFRO without AS and IEX was limited, due to high hardness of the feed water (TH = 2.96 mmol L^{-1}) to 14 %, which led to the necessity of a high feed flow, and thus, 24 vessels (each containing three elements) were required to comply with maximum feed flow limitations. Although this study did not focus on energy demand, it should be noted that this configuration has by far the highest energy demand since the largest feed volume has to be pressurized. Single-stage PFRO with AS dosing, in a classical design 6-m PV, achieved a recovery of 60 % limited by the minimum concentrate flow. By using 8-m PV the feed flow can be split to one PV less, increasing the concentrate flow per vessel. This shifts the concentrate flow limitation to a higher RO recovery (66 %). Concentrate recirculation could further increase the recovery of single-stage PFRO, but was not considered in this study, among other things due to concerns regarding the prediction of scaling.

Two-stage PFRO in a classically staged array of 2:1, with 6 PV (each equipped with 6 elements) in the first and 3 PV in the second stage showed for both configurations, with AS dosing and with IEX as pretreatment, a maximum system RO recovery of 82 %, due to minimum concentrate flow limitation in the 2nd stage. Reducing the vessels in the second stage to 2 PV, each equipped with 8 elements, increased the achievable RO recovery to 86 % for the IEX-PFRO,

Table 2. Maximum RO- and system recovery, limitations for different systems and configurations, average fluxes, and number of elements for all systems with a defined product permeate flow of $Q_P = 50\,m^3h^{-1}$.

System	Configuration		Q_F [m^3h^{-1}]		ϕ_{RO} [%]	Limitation	ϕ_{System} [%]	Average flux [$L\,m^{-2}h^{-1}$]	Elements [–]
	PV × elements [–]	2 ppm AS or IEX	$Q_{F,raw}$	$Q_{F,RO}$					
Single-stage PFRO	24×3	–	357	357	14	*LSI* > 0 and $Q_{F,max}$	14	18.67	72
	9×6	with AS	83.3	83.3	61	$Q_{C,min}$	61	24.9	54
	7×8	with AS	75.8	75.8	66	$Q_{C,min}$	66	24	56
Two-stage-PFRO	6×6 + 3×6	with AS	61	61	82	$Q_{C,min}$ 2nd stage	82	24.9	54
	6×6 + 3×6	IEX conventional regeneration	63.5	61	82	$Q_{C,min}$ 2nd stage	79	24.9	54
	6×6 + 2×8	IEX conventional regeneration	60.4	58.1	86	$Q_{C,min}$ 1st stage	83	25.9	52
	5×8 + 2×8/2×7	with AS	59.5	59.5	84	*LSI* > 2.15	84	24/24.9	56/54
	5×8 + 2×8/2×7	IEX conventional regeneration	59.8	57.5	87	$Q_{C,min}$ 2nd stage	84	24/24.9	56/54
	5×8 + 2×8/2×7	IEX complete substitution	57.5	57.5	87	$Q_{C,min}$ 2nd stage	87	24/24.9	56/54
CCRO	13×4	with AS**	60.5 (57*)	60.5 (57*)	84 (89*)	*LSI* > 2.15–2.55	83 (88*)	25.9	52
	13×4	IEX conventional regeneration	56.6 (54.7*)	54.4 (52.6*)	92 (95*)	SiO_2 scaling; p_{max}	88 (91*)	25.9	52
	13×4	IEX partly substitution	56.2 (54.3*)	54.4 (52.6*)	92 (95*)	SiO_2 scaling; p_{max}	89 (92*)	25.9	52
	13×4	IEX complete substitution	55.2 (53.4*)	54.4 (52.6*)	92 (95*)	SiO_2 scaling; p_{max}	90 (94*)	25.9	52

*Numbers in brackets indicate the upper recovery, i.e., temporary supersaturation of the solution (only possible for CCRO); **CCRO with AS is dimensioned on $Q_{P,CCRO\text{-}AS.} = 50.8\,m^3h^{-1}$ due to considered extended flushing (cf. Sect. 4.2).

whereas the two-stage RO with AS was then limited to 84 % by $CaCO_3$ scaling. Even higher recoveries may be feasible for the IEX-PFRO by reducing the PV number in the first stage as well, and thus, increasing the concentrate flow per vessel. By implementing 8-m PV for both stages, the maximum RO recovery increased to 87 %. Furthermore, by implementing 7-m PV in the 2nd stage, the number elements can be reduced, reaching the same recovery and still complying with the maximum flux restriction, thus, offering a better membrane utilization. However, it should be noted that this element reduction increases the lead element flux and is only advisable if the risk of (biological) fouling is low as in this presented study.

Except for single-stage PFRO without AS dosing and two-stage PFRO with AS dosing and 8 element design, all PFRO configurations were limited by the minimum concentrate flow, and therefore by hydraulics. One might claim that a lower chosen limit for the minimum concentrate flow, e.g., $3\,m^3h^{-1}$ (design specification with $SDI_{Feed} < 3$), would further increase the RO recovery, but this certainly increases the likelihood of concentration polarization and its associated negative effects. Moreover, the limitation would be still given by the minimum concentrate flow at a slightly higher recovery (+2 %).

The use of IEX as pretreatment for PFRO systems proved to be only beneficial (with respect to the system recovery) when complete substitution is applied as IEX-regeneration strategy, which is shown in Tab. 2 for the 8-m PV design. In case of conventional regeneration strategy, the system recovery is even lower compared to the operation without IEX, due to the additional water required to regenerate the IEX. This is primarily due to the hydraulic limitation of PFRO systems. Therefore, the gained advantage of the IEX as pretreatment to increase the recovery without scaling limitation cannot be facilitated.

Although the standard staged-array configuration for inland BWRO is 2:1 with 6-m PV equipped with 6 elements each, different configurations with 7- and 8-m PV were proposed, which are primarily used in single-stage SWRO applications [30]. Since the minimum concentrate flow was identified as the main restriction for the exemplary water composition, deviations from classical BWRO configuration might be in some instances advisable to reduce the hydraulic limitations. Additionally, using less PV might decrease investment costs [30].

4.2 Performance of CCRO Systems

The achievable RO recovery in case of a CCRO system without AS dosing or without IEX pretreatment is low ($CaCO_3$ scaling equal to PFRO without AS or IEX, cf. Sect. 4.1), which results in short and non-feasible (filtration) cycle times. To increase the cycle time a high system volume would be required, which would on the other hand extend the flushing time to an uneconomic level. Therefore, CCRO without AS dosing or without IEX was excluded here but might be applicable for a feed that is less prone to scaling.

All considered CCRO configurations were designed with 13 PV (6 m, equipped with 4 elements and operated at $\phi_{CC} = 50\,\%$). The blank space in each PV increased the system volume to $\sim 1.9\,m^3$, which enabled a practicable cycle and flushing time.

A volume of $8\,m^3$ in 10 h was assumed to be feasible for the extended flushing for all CCRO configurations. For conventional and partial substitution regeneration strategy, the volume for extended flushing is reused for rinsing and reverse exchange. Thus, no additional water has to be softened. However, for complete substitution strategy, this volume has to be produced in excess by IEX softening. For the CCRO with AS, the extended flushing volume is provided by excess production of permeate based on:

$$Q_{P,\ CCRO\ AS} = Q_P + Q_{Ext.\ Fl.} = 50 m^3/h + 0.8\ m^3/h \tag{6}$$

CCRO configuration with AS dosing was limited by $CaCO_3$ scaling to a recovery of $\phi_{RO} = 84\,\%$. Dhakal et al. showed stable conditions of a comparable RO concentrate with AS dosing ($2\,mg\,L^{-1}$) for $SI = 2.55$–2.65 without nucleation induction for ~ 4 h in air-tight reactors [12]. Therefore, SI of 2.55 was assumed to calculate the upper RO recovery ($\phi_{RO} = 89\,\%$). The necessary excess production of permeate for extended flushing reduces the system recovery by 1 %.

Fig. 2 depicts an exemplary result for the quantity balance in a hybrid IEX-CCRO system with an upper RO recovery ($\phi_{RO} = 95\,\%$; $\phi_{System} = 91\,\%$) and conventional regeneration (i.e., no substitution by RO concentrate). Regeneration streams are shown as dashed lines. Since regeneration was simulated with an operation time of 10 h, the regeneration is shown as flows per 10 h.

With RO recoveries of 92 to 95 % the hybrid IEX-CCRO configurations showed the highest recoveries. The recovery of 92 % is due to limitation by SiO_2 saturation, and the upper recovery of 95 % due to the maximum pressure restriction (20 bar). Even at 95 % recovery ($CF = 20$) the calculated nucleation induction time of SiO_2 of about 1.5 days is not in the least achieved by the cycling time.

Interestingly, none of the CCRO configurations were limited by hydraulics, which can be primarily explained by the circulation pump that enables higher flows and prevents minimum concentrate flow restriction (main limitation of PFRO configurations). This allows CCRO systems to achieve higher recoveries. Since the $CaCO_3$ limitation was (nearly) eliminated in the IEX-CCRO, this configuration was able to exploit the gained advantages of the IEX much more than the IEX-PFRO. In general, the hydraulic advantages of the CCRO allowed the best membrane-surface utilization (the PFRO with 8-m PV in the 2nd stage reached the same flux, but with lower recovery). However, when calculating the cost, it is crucial to consider that for CCRO the PVs are usually only partly filled to operate with feasible cycle times [20]. Thus, more PVs are needed, which might result in higher investment costs [30]. Nevertheless, if a reduction in the number of PV is required, a possible configuration for the CCRO with 11 PV (6 m), each equipped with 5 elements (then with a lower flux), would be feasible, too.

4.3 Supplementing NaCl by Using RO Concentrate as IEX Regenerate

As explained above, a higher RO recovery results in smaller IEX units. When comparing conventional IEX-PFRO (with 6 m PV) and IEX-CCRO (with upper RO recovery), the latter system saves 15 % of both resin and NaCl solely since less feed is needed. Moreover, less wastewater is produced in the regeneration process.

To discuss the potential of supplementing NaCl by using RO concentrate as IEX regenerant, the IEX-CCRO (upper recovery) with complete regeneration substitution was selected. Considering the specific consumption of 180 $g_{NaCl}L_{resin}^{-1}$, a total amount of 373.5 kg NaCl (~147 kg Na^+) is required to regenerate the IEX. In 10 h operation, this system configuration produces 26 m^3 concentrate with a Na^+ concentration of 3152 $g\,m^{-3}$. This is an equivalent of ~82 kg Na^+, which represents ~55 % of the Na^+ demand for the IEX regeneration. However, the applied NaCl regeneration solution needs a high concentration to overcome the higher selectivity of the TH towards Na^+ (approx. 2.5 times higher selectivity of Ca^{2+} compared to Na^+ [5]). With the defined volume for the reverse exchange (2.15 BV), approximately 4.5 m^3 of the concentrate can be applied, which is equivalent to 14.3 kg Na^+ that can substitute ~10 % of NaCl demand.

NaCl supplement could be further increased by applying a higher volume for the reverse exchange, i.e., expanding the dilution. This could be an option since lower concentrations down to 3 % are described in the literature, e.g., [5]. Moreover, Vanoppen et al. [31] extrapolated (from experimental data) in a comparable configuration that a 3.5-% NaCl solution is sufficient for 100 % resin regeneration. Considering a NaCl concentration of 5 %, a volume of 7.5 m^3 (~3.5 BV), which represents roughly 24 kg Na^+, could supplement NaCl by a little more than 15 %. This demonstrates that even at a high recovery and lower reverse exchange solution concentration the supplement potential is relatively small because of the necessity to regenerate with approx. 200 % (~180 $g_{NaCl}L_{resin}^{-1}$) excess of Na^+ to TH (considering the equivalent concentration).

Fig. 3 shows the charge equivalent flows for Na^+ and TH in complete substitution IEX-CCRO system (upper recovery) during the operation time of 10 h. It should be noted that the additional 8 m^3 for extended flushing are not considered for desalination in the CCRO, but it is solely used for flushing the CCRO and subsequently for the IEX regeneration.

Using RO concentrate for the backwash might cause an initial partial regeneration of IEX. For instance, Vanoppen et al. [31] regenerated an IEX to approx. 40 % of its capacity using RO concentrate (from softened tap water as feed source). However, backwash is typically applied with high flow velocities and thus reverse exchange during backwash is not considered here. If (partial) regeneration by backwash with RO concentrate is attainable, the remaining concentrate volume (10 m^3) could be used for this purpose and thus further reduce the required NaCl demand.

Regenerating IEX with RO concentrates can cause unwanted reactions in the IEX. In particular, high HCO_3^- and SO_4^{2-} concentrations, along with a relatively high pH ($\approx$ 8.4) of the concentrate in the given example, might lead to precipitation when Ca^{2+} and Mg^{2+} are reverse exchanged. PhreeqC simulation of the reverse exchange showed that dolomite and calcite are most likely to precipitate due to high supersaturation (*SI* of 6 and 3, respectively), which

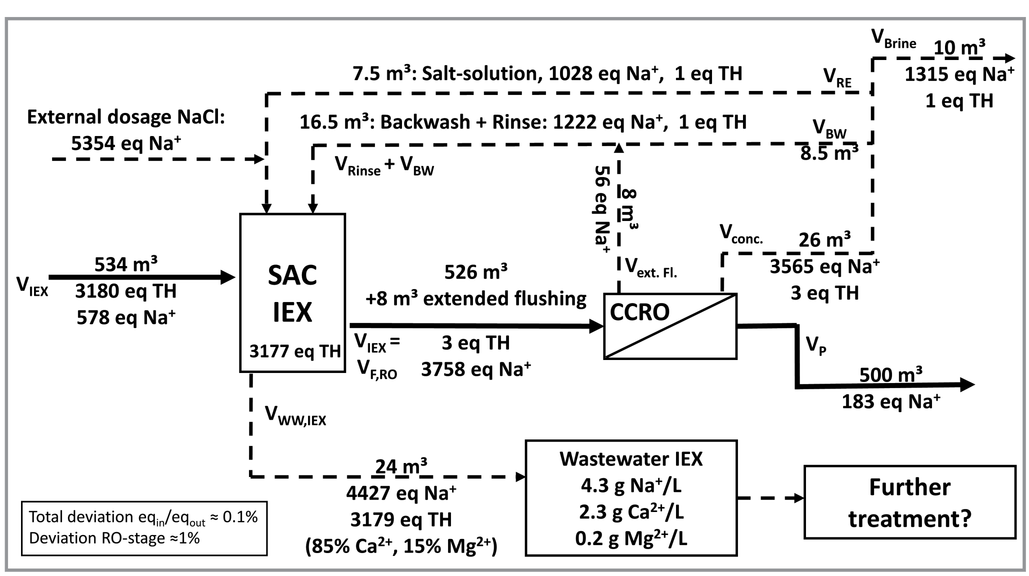

Figure 3. Schemes for charge equivalent flows of Na^+ and TH in complete substitution IEX-CCRO system during the operation time of 10 h (note that $V_{ext.\,Fl.}$ = V_{Rinse}). Deviation of equivalents in RO stage due to iterration of LewaPlus.

might lead to unwanted precipitation inside the IEX, causing operational problems. This might be overcome by implementing an upflow rinse with higher velocities to fluidize the resin and washing-out the precipitates while holding back the resin, as, e.g., described in [15]. Moreover, the high supersaturation might enable a controlled and selective precipitation to separate Ca^{2+} and Mg^{2} from Na^{+}, e.g., in a precipitation reactor with seeding crystals.

Generally, Fig. 3 shows that the IEX wastewater had the highest potential to further reduce the amount of NaCl demand and to approach a self-sustaining process (after an initial NaCl dosage) since the stream has by far the highest Na^{+} equivalent load (excluding the dosed NaCl). Suitable further treatment of the IEX wastewater might be nanofiltration (NF) to separate Na^{+} from the divalent Ca^{2+} and Mg^{2+}. The feasibility of NF treatment for IEX wastewaters was reported in [32], where NF270 (DuPont) membranes were used, with rejections of approx. –2 %, 60 % and 75 % for Na^{+}, Ca^{2+} and Mg^{2+}, respectively. This option might especially be suitable for the proposed hybrid IEX-CCRO system since the volume to treat is relatively low. Further on, the NF can be operated while the 10 h operation time of the IEX-CCRO, making a sequencing-batch NF applicable, which treats subsequent the permeate of the previous run. Thus, the NF system could be designed relatively small.

5 Conclusion

This study opens options to increase the recovery of inland BWRO and potentials to avoid the dosage of AS. Three systems, conventional single- and two-stage PFRO, as well as CCRO in different configurations (different number of elements in series per PV, CCRO with/without temporary supersaturation of the solution in the cycle, and hybrid PFRO as well as CCRO with IEX pretreatment for softening or AS dosing), were designed, simulated, and compared with respect to the required number of elements and the quantity of raw feed and brine to be discharged. The systems were simulated with real water matrix (hard feed water) and fixed permeate production using LewaPlus (Lanxess). The main findings (considering the exemplary feed water) are:

- Conventional PFRO (single and two-stage with 6 m PV) was predominantly limited by hydraulics.
- Implementation of 8-m PV can increase the recovery of PFRO by mitigating the hydraulic limitation and might furthermore improve the economic efficiency.
- IEX pretreatment enabled operation without AS dosing at the same RO recovery (PFRO), or higher RO recovery (CCRO) compared to the respective system with AS dosing.
- IEX pretreatment necessitates additional water for its regeneration. In the case of IEX-PFRO, conventional regeneration yielded in lower system recovery than with AS dosing.
- Substitution of regenerate water with RO concentrate increases the system recovery.
- CCRO exhibited no hydraulic limitations, which allowed higher recoveries and a better utilization of the membrane surface (higher average flux, fewer elements).
- The novel proposed IEX-CCRO with and without temporary supersaturation of the solution in the cycle achieved the highest system recovery (up to 94 % in case of complete regeneration substitution by RO-concentrate).
- Substitution of regeneration with RO concentrate furthermore reduces the demand for regeneration salt (NaCl). However, the potential of RO concentrate is limited. Higher potential to supplement NaCl is found in the IEX wastewater, which could be further treated, e.g., by precipitation and/or NF to separate TH from Na^{+}.

CCRO is a promising option for inland desalination offering high recoveries with small-footprint one-stage systems with presumable higher resistance towards scaling and minute hydraulic limitations. However, more experimental data is needed to verify the concept of undershooting the nucleation induction time and to investigate strategies for efficient flushing in practical applications to impede scaling. Moreover, the long-term effect of the system inherent periodically changing hydraulic pressure on the durability, e.g., the membranes and pumps, which are usually designed on a specific pressure range has to be clarified [22]. Finally, it should be emphasized that the main disadvantage of hybrid IEX-RO/CCRO systems is the added salinity of the wastewater streams from the IEX and the RO. Therefore, e.g., in Germany, NaCl is not approved as a regeneration solution for IEX in centralized drinking watertreatment systems. However, the proposed IEX-CCRO concept could be a feasible system if high recoveries are required, and zero-liquid discharge is an objective (e.g., industrial water treatment). The integration of cascade NF and/or controlled precipitation for the IEX wastewater can separate TH from Na^{+} and further reduce the wastewater volume. Subsequent thermal treatment could enable a self-sustaining system with nearly zero-liquid discharge. Implementing such further treatment steps could alleviate the ban on NaCl as regenerate for municipal water supplies, since no salts would be discharged and thus might offer an alternative without the need for AS.

This research was conducted in the framework of the project KonTriSol (*https://kontrisol.de/*). The Project KonTriSol is funded by the Federal Ministry of Education and Research of Germany (BMBF) and co-financed by the German Technical and Scientific Association for Gas and Water (DVGW). Open access funding enabled and organized by Projekt DEAL.

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DOI: 10.1002/cite.202100042
URN: urn:nbn:de:hbz:464-20210902-123638-2