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Citation	F. Du et al. “Sodium hydroxide production from seawater desalination brine: process design and energy efficiency,” Environmental Science & Technology, 52, 10 (April 2018): 5949–5958 © 2018 American Chemical Society
As Published	http://dx.doi.org/10.1021/acs.est.8b01195
Publisher	American Chemical Society (ACS)
Version	Author's final manuscript
Citable link	https://hdl.handle.net/1721.1/123096
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F. Du, D.M. Warsinger, T.I. Urmi, G.P. Thiel, A. Kumar, and J.H. Lienhard V, “Sodium hydroxide production from seawater desalination brine: process design and energy efficiency,” *Environmental Science & Technology*, **52**(10):5949–5958, 18 April 2018.

Resource recovery from desalination brine: energy efficiency and purification process integration for sodium hydroxide production

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ABSTRACT

The ability to increase pH is a crucial need for desalination pretreatment (especially in reverse osmosis) and for other industries, but processes used to raise pH often incur significant emissions and non-renewable resource use. Alternatively, waste brine from desalination can be used to create sodium hydroxide, via appropriate concentration and purification pretreatment steps, for input into the chlor-alkali process. In this work, an efficient process train (with variations) is developed and modeled for sodium hydroxide production from seawater desalination brine using membrane chlor-alkali electrolysis. The integrated system includes nanofiltration, concentration via evaporation or mechanical vapor compression, chemical softening, further ion-exchange softening, dechlorination, and membrane electrolysis. System productivity, component performance, and energy consumption of the NaOH production process are highlighted, and their dependencies on electrolyzer outlet conditions and brine recirculation are investigated. The analysis of the process also includes assessment of the energy efficiency of major components, estimation of system operating expense and comparison with similar processes. The brine-to-caustic process is shown to be technically feasible while offering several advantages, i.e. the reduced environmental impact of desalination through lessened brine discharge, and the increase in the overall water recovery ratio of the reverse osmosis facility. Additionally, best-use conditions are given for producing caustic not only for use within the plant, but also in excess amounts for potential revenue.

INTRODUCTION

As the global population grows and economies develop, demands on the world's fixed fresh water supply are increasing. Both the growing demand and regional water stress—often punctuated by a changing climate—are driving the rising use of seawater desalination to access the 97% of Earth's water found in the oceans.[1] With considerable reductions in energy consumption and cost over the past several decades, the dominant choice for new seawater desalination facilities is reverse osmosis (RO).[2]

Due to the implementation of more energy-efficient pumps and improved membranes, RO processes are coming closer to the thermodynamic minimum energy consumption.[3,4] Despite these technological advances, however, seawater RO (SWRO) – and all desalination systems currently in use today – produce a large quantity of concentrated brine that is discharged back to the sea.[5] This discharge has been reported to threaten marine ecosystems[6] in several ways, including upsetting the physiochemical balance, causing thermal plumes, and amplifying contaminant concentration.[7] One class of solutions to this problem involves more extensive brine post-treatment, possibilities for which have been comprehensively reviewed elsewhere.[8-10] For instance, zero liquid discharge (ZLD) has been considered as a way to eliminate brine discharge. ZLD, however, presents high energy and capital costs,[11] largely as a result of the high concentrations which require energy intensive thermal desalination technologies.[12-15] The reuse of the brine to produce useful and valuable chemicals can be a more sustainable solution, although this approach is rarely applied due to the variety of impurities in the brine, leading to complex separation and purification needs.[16] Nevertheless, such a solution could limit harmful environmental impacts by reducing (or even eliminating) brine discharge; and this approach could cut plant costs or generate revenue, making fresh water more affordable.[17]

In this study, we focus on one example of brine chemical recovery: converting NaCl in brine to NaOH, commonly known as caustic or caustic soda, which can be re-used within the RO facility. NaOH is widely used to increase pH during pretreatment of seawater feed. At higher pH, aqueous boron compounds, toxic to human[18] and plant[19,20] health, exist primarily as charged borate species, which are better rejected by RO membranes.[21,22] Undesirable heavy metals and hardness, which can cause membrane scaling, can also be precipitated at high pH.[23,24] The use of caustic soda can hinder biofouling as well.[25] Further, caustic soda is used in the makeup of cleaning solutions for removing organic foulants and scales.[26] Converting RO brine to NaOH therefore can benefit both the environment and the financial bottom line by reducing brine discharge while simultaneously supplying in-plant chemical demand. Excess caustic soda produced might even be a profitable side-product of high-capacity seawater desalination plants: world annual consumption of NaOH is constantly growing, from 53 million tons in 2002 to over 65 million tons in 2015 and 82 million tons in 2020 (expected).[27,28]

The vast majority of NaOH used in RO plants today is manufactured by the chlor-alkali process, which accounts for 99.5% of caustic production worldwide.[28] The process electrolyzes near-saturated NaCl brine, producing caustic soda as well as chlorine and hydrogen gas. Three main variants of the process exist, but the membrane variant, which uses a cation exchange membrane as the separator between catholyte and anolyte, is the most widely used and is considered the best available technology.[29,30] Membrane electrolyzers produce caustic soda of 32-35 wt% concentration, but the process requires a very pure feed brine of about 290-310 g/L NaCl concentration.[31] The major purity requirements are listed in the following:[28,31-33]

- Hardness ions (Ca^{2+} + Mg^{2+}) < 0.02 ppm, as Ca^{2+} reduces current efficiency and both ions increase electrolyzer operating voltage;
- Free chlorine (chlorine and its active hydrolyzed forms, i.e. hypochlorite[33] < 0.1 ppm, as it damages ion-exchange resin (used for pretreatment) and reduces life of equipment and piping;
- Sulfate as Na_2SO_4 < 4-8 g/L, as they reduce current efficiency of the electrolyzer.

These stringent purity requirements, particularly on hardness (< 0.02 ppm for Ca^{2+} and Mg^{2+}), indicate that any RO-brine reused will require considerable treatment before being suitable for the chlor-alkali process.

Previous studies have suggested alternative approaches to treat seawater and/or its concentrated brine to obtain NaCl as intermediate product and ultimately to produce NaOH.[34,35] Others have focused more on the process of converting brine directly to a chlor-alkali feed without going through the intermediate stage of salt production.[36,37] Thiel et al.[38] provide a more detailed review of these and other technologies, along with thermodynamic benchmarks for each technology.

Beyond these past studies, no comprehensive model has been found in the literature that describes a full system to convert RO brine to caustic soda, including pretreatment and production. By combining the individual components, interrelations between components are to be considered and model parameters are to be chosen and optimized in order to fit the whole system for caustic production directly from seawater. In this work, an Aspen Plus® model for the brine-to-caustic system, including purification and concentration components and membrane electrolysis cell, is constructed. Using the model, system productivity and the energy consumption of each component are determined.

In the section “Modeling methodology,” we introduce the overall modeling approach, system physics and the models employed for each component. In the section “System Parameterization, boundary Conditions,” we present and justify the values used to parameterize the components. In the section “Results and discussion,” we discuss the results from the model and the advantages of the process. Finally, the environmental implications of the present process are considered in the last section.

MODELING METHODOLOGY

In this section, we first introduce the modeling approaches and assumptions made. Thereafter we describe the process chain and its individual components to convert SWRO brine to caustic soda. To achieve the desired purification and concentration for the membrane electrolysis, essential pretreatment components are chosen based on their reliability and maturity.

MODELING APPROACH AND ASSUMPTIONS

Steady-state simulations in Aspen Plus are conducted with the focus on system-level performance of the conversion process. Details at the component-level (i.e., heat and mass transport phenomena, reaction kinetics) are not taken into consideration.

The ENRTL-RK model, which is implemented in Aspen, is applied to simulate the non-ideal thermodynamic behavior of brine and other relevant electrolyte streams. This model combines ENRTL (Electrolyte non-random two-liquid) model for the non-ideal electrolyte liquid phase and the Redlich-

Kwong (RK) equation of state for the gas phase. Originally developed by Chen[39], the ENRTL model is a widely applied property model for process simulation of electrolyte systems with mixed solvent. Song and Chen[40] concluded that the ENRTL is preferred for process modeling applications, compared to other models (Pitzer, OLI MSE, UNIQUAC). In Aspen Plus, the improved ENRTL model from Song and Chen[40] is implemented.[41]

The following assumptions are made during the modeling:

- Seawater is considered as NaCl solution, contaminated with Ca^{2+}, Mg^{2+} (hardness ions), bromide (Br^{-}) and sulfate ions (SO_4^{2-});
- Each stream is ideally mixed without temperature, pressure and concentration gradients;
- Chemical equilibria of aqueous phase reactions, including electrolyte dissociations and salt precipitations, are reached for every stream. These equilibria are predicted automatically by Aspen.

OVERALL PROCESS CHAIN

Figure 1 shows a block flow diagram with relevant components and streams: the SWRO brine is first purified by nanofiltration (NF) where most sulfate ions and a fraction of hardness ions (Ca^{2+} and Mg^{2+}) are removed. The NF permeate is concentrated by electrodialysis (ED), and further concentrated by evaporation or mechanical vapor compression up to NaCl saturation, as required by the electrolyzer. The remaining hardness ions in the brine are removed by chemical softening and ion exchange (IX). Finally, the sufficiently pure and concentrated brine is acidified and sent to the membrane electrolyzer to produce the products: NaOH, Cl_2, and H_2.

Nanofiltration (green box in Figure 1) is used to remove sulfate ions. High concentration of sulfates may cause $CaSO_4$ fouling[42] in concentration units (ED, Evaporation). This explains why NF is put at the first step in the process chain. In addition, NF lowers Ca and Mg content of the brine,[43,44] reducing other fouling concerns.[45]

Electrodialysis (orange box in Figure 1) is chosen as the next step for a primary concentration. The employed NF-ED chain is also suggested by Garriga,[36] and ED is also recommended by Casas et. al.[17] The feed is split into two streams which are fed into a diluate and a concentrate channel. ED stack transports NaCl (and water) from the former to the latter. For industrial ED systems, the highest concentration achieved is around 200 g/kg (20 wt%).[46] The diluate outlet is set as 3.5 wt%. This outlet concentration corresponds to normal seawater and allows the ED diluate to be recycled as a feed into the RO plant.

Since the membrane cell requires nearly saturated brine, evaporation is used after ED as a final concentration step (pink box in Figure 1). The combination of ED and evaporation might be considerably more economic than evaporation alone, as suggested by Leitz.[47]

Mechanical vapor compression (MVC) is an alternative for evaporation. While the evaporator is simply heat-driven, MVC compresses the vapor produced by evaporation and powers the evaporator using this compressed vapor. With a preheating heat exchanger integrated, the only energy input is the mechanical work associated with the compressor.

After being concentrated to saturation, the brine goes through the chemical softening stage. Na_2CO_3 and NaOH are added to precipitate Ca^{2+} and Mg^{2+} ions as calcium and magnesium salts. These precipitates are then removed by filtration.

Chemical softening achieves a ppm-level hardness level which still does not meet the required purity for the electrolyzer cells.[28] Thus, a cation ion-exchange step is used as a final purification step to remove hardness down to ppb-level. The process chain of chemical softening, ion-exchange and electrolysis is a standard process in a typical membrane chlor-alkali plant.[28] Before entering the electrolyzer, the purified brine is acidified with HCl.

In the membrane electrolyzer, production of Cl_2, H_2, and caustic soda takes place, resulting in a depleted brine stream that typically contains up to 20 wt% NaCl. The depleted brine from the electrolysis cell must be dechlorinated (light blue component in Figure 1) before being discharged to the environment[29] or recycled.[28]

After dechlorination, the depleted brine is fed into a splitter and split into a purge stream (see “Purge stream” in Figure 1, mid left) and a recycled stream. The purge stream leaves the system. We define the ratio of the purged stream and the total stream fed to the splitter as the “purge ratio”. The role of the purge is to prevent impurities (primarily sulfate) from accumulating in the system (see section “Purge ratio”). This is also mentioned by the literature[28] as one of the methods to control sulfate. Other possible sulfate removal/controlling methods would be an additional NF stage or the usage of barium salts in chemical softening. However, the former leads to NaCl depletion[48] and the latter involves the usage of expensive and toxic barium salts.[29] Thus, both options are not favored here.

The recycle stream has a brine concentration of around 20 wt%[28] and does not require the primary concentration of ED, so it is fed back to the evaporation/MVC component.

MODELING OF MEMBRANE ELECTROLYZER

The ion-exchange membrane in the electrolyzer separates the electrolysis cell into anode and cathode chambers. The overall reaction is (R1). On the anode, chloride is oxidized to chlorine via (R2). On the cathode, water is reduced to hydrogen and hydroxide ions according to (R3).

Overall
$$2\mathrm{NaCl} + 2\mathrm{H_2O} \xrightarrow{\mathrm{Electrolysis}} 2\mathrm{NaOH} + \mathrm{H_2} + \mathrm{Cl_2} \qquad \text{(R1)}$$

Anode:
$$2\mathrm{Cl^-} \longrightarrow \mathrm{Cl_2} + 2\mathrm{e^-} \qquad \text{(R2)}$$

Cathode:
$$2\mathrm{H_2O} + 2\mathrm{e^-} \longrightarrow \mathrm{H_2} + 2\mathrm{OH^-} \qquad \text{(R3)}$$

A typical membrane electrolysis cell is illustrated in Figure 2. On the anode (blue), chloride is oxidized to chlorine gas, part of which is dissolved in the anolyte.[49] The side reaction is water oxidation, producing oxygen. Extents of both reactions depend on the process chlorine efficiency ξ^{P} and the anode current efficiency ξ.[50] The definition of these efficiencies is elaborated in the Supplementary Information (SI) section “Anode chamber.” On the cathode (red), water is reduced to hydrogen, producing hydroxide ions. Part of them migrates back to the anolyte, reducing the sodium transport by a factor of η, the cathode current efficiency (see SI section “Cathode chamber and membrane transport”). Typically, the anode side brine has depletion of NaCl from 26 wt% to 20 wt% and the feed caustic concentrates NaCl from 30 wt% to 32 wt%. Some of the 32 wt% caustic is taken as product; the rest is slightly diluted to 30 wt% using deionized water and recirculated.

The detailed Aspen modeling for the electrolyzer is elaborated in the SI section “Modeling of membrane electrolyzer in Aspen Plus”. Additionally, model validation is conducted against a set of reference plant data in the literature[28], which is described in SI section “Validation of membrane electrolyzer model”. The agreement with literature values shows the accuracy of the electrolyzer model and the applied thermodynamic property model.

ENERGY CONSUMPTION

The energy consumption of the electrolyzer can be calculated as follows:

$$\dot{W}_{\mathrm{cell}} = U_{\mathrm{cell}} \cdot I_{\mathrm{cell}} = U_{\mathrm{cell}} \cdot F \cdot \frac{\Delta \dot{n}_{\mathrm{NaOH}}}{\eta} \tag{1}$$

The cell voltage, U_{cell}, is assumed constant at 3.2 V, a value taken from reference plant data given in the literature.[28] It shall be noted that in real cells, the cell voltage increases with increasing current due to the ohmic loss in the cell and the over-voltage on both electrodes.[28]

MODELING OF OTHER COMPONENTS

The modeling of other components used in the process chain, including brine acidifier, ion-exchanger, chemical softening, evaporator, MVC, electrodialysis, nanofiltration, dechlorination and brine purge, are elaborated in the Supplementary Information (SI) section "Modeling of other components in Aspen Plus".

SYSTEM PARAMETERIZATION, BOUNDARY CONDITIONS

In this section, the feed brine composition is given as a boundary condition of the model. Parameter values used in each individual component of the Aspen modeling are listed in Table 1. More details including parameters of individual components are given in Table S6 of the SI.

RESULTS AND DISCUSSION

This section introduces the results obtained by this study. First, we evaluate the energy consumption and thermodynamic efficiency of each component and give some suggestions for system improvement. Next, we show the dependency of system performance on two important process parameters based on a sensitivity study and justify our chosen parameter values. Then, we use the obtained chemical dosage requirements and energy consumption numbers to estimate the operating expense (OPEX) of the system and compare it with standard chlor-alkali. Last, we discuss the advantages, best-use examples, and challenges of the proposed process.

OVERALL PRODUCTIVITY

From 17.5 t/h brine feed to the process, the membrane electrolyzer produces 208.4 kg/h of 32 wt% NaOH (66.7 kg/h as equivalent dry product). While 1.9 kg/h of it (around 3 %) should be used internally for the chemical softening and ion-exchange components, the real caustic output amounts to 64.8 kg/h (as dry). A summary of mass flows at each stage can be found in Table S7 of the SI. The model is scalable with mass, thus allowing its application to a different NaOH production rate.

ENERGY CONSUMPTION AND SECOND LAW EFFICIENCY OF COMPONENTS

In industry, energy costs dominate the chlor-alkali process and most high-concentration processes. For this process chain, the energy consumption, least work, and second law efficiencies of various components are illustrated in Figure 3.

Notably, two options are given for the brine saturation component: the evaporator or the MVC. The evaporator consumes 190.8 kW heat (2.94 kWh/kg NaOH) whereas the MVC component consumes 15.75 kW electricity (0.24 kWh/kg NaOH). Regardless of this concentration component, the rest of the system (NF, ED, electrolyzer) consumes about 189.9 kW (2.93 kWh/kg NaOH) electricity.

The second law efficiency, given by Equation (2), is a quantitative measure for the thermodynamic efficiency of a given process. Equation (2) can be applied for processes including both work $\dot{W}$ and heat input $\dot{Q}$:[56,57]

$$\eta_{\mathrm{II}} = \frac{\dot{W}_{\mathrm{least}}}{\dot{W} + \left(1 - \frac{T_\infty}{T_Q}\right) \cdot \dot{Q}} \tag{2}$$

where T_∞ is the ambient temperature, and T_Q is the temperature of the heat source (both in K). In the evaporator, we assume the use of 1.2 bar saturated steam (123.5 °C) as the heat source, which is reasonable condition for industrial waste steam. $\dot{W}_{\mathrm{least}}$ is the thermodynamic least work. Its calculation is elaborated in the SI (equation S-10).

The chlor-alkali electrolysis consumes the most energy in the process. However, it shows good thermodynamic efficiency (68.2 %), limiting potential improvements. Irreversibilities are mainly caused by limited current efficiency and voltage losses (due to overvoltages on the electrodes and the ohmic losses in the solution, the membrane, and the metal hardware).[28] Nevertheless, this efficiency assumes that Cl_2 and H_2 are desired products beside NaOH. If, instead, NaOH is the only product of interest and HCl is produced as side product (by combusting H_2 and Cl_2), the chlor-alkali electrolysis efficiency decreases to 39.4 % when no energy is recovered from the formation of HCl.

The evaporator, as the second highest energy consumer in the process, shows a poor second law efficiency (3.5 %). Better use of the steam produced (i.e., to preheat before the electrolyzer) would increase the efficiency of this component significantly.

Overall, improvement of the energy efficiency of brine concentration components represents the most feasible route to significant energy savings. Processes not requiring as much brine concentration as electrolysis could yield very significant energy savings.[38,58]

SENSITIVITY STUDIES

Modeling of the brine-to-caustic process in Aspen allows the variation of certain parameters to reveal their impact on the system performance. The key parameters from the process chain chosen here are the anolyte outlet concentration of the electrolyzer (depleted brine in Figure 2) and the “purge ratio” of the recycling brine (Figure 1, after the dechlorination block). During the sensitivity study, all system parameter values (see Table 1) are kept constant except for the varied parameter.

ANOLYTE OUTLET CONCENTRATION

System performance is heavily influenced by the concentrations of streams related to the recirculation of depleted brine from the electrolyzer back into the concentration stages. A lower anolyte outlet concentration corresponds to a higher conversion of NaCl to NaOH in the electrolyzer cell, and therefore high caustic productivity. However, this requires that the recycled brine must be concentrated more, resulting in a higher absolute energy consumption in the evaporator/MVC component. This high absolute energy consumption is offset by the higher caustic productivity in the electrolyzer. Overall, the electrolyzer productivity wins this competition: the specific energy consumption, normalized by the caustic production is lower at low anolyte outlet concentrations, as shown in Figure 4.

It is evident from Figure 4 that by lowering the anolyte concentration from 22 wt% to 18 wt%, the evaporator/ MVC component is consuming about 10% less specific energy. Technically, this means a high applied current and a great depletion of the feed NaCl in the electrolysis cell are beneficial for the whole brine-to-caustic process in terms of productivity and energy consumption. However, as shown in Figure 4, a lower limit exists at 18.2 wt% (200 g/L), below which a stable operation of the membrane electrolyzer cell is no longer feasible.[28]

Based on the results of this sensitivity study, we chose 19 wt% as the anolyte outlet concentration of the electrolyzer (Table 1) which allows high system productivity at low specific energy consumption while avoiding the danger of unstable operation by providing a safe margin between the operation point and the lower limit.

PURGE RATIO

Purging refers to removing a fraction of the depleted brine from the system using a simple splitter, allowing only a remaining fraction to reenter the process (see Figure 1). This prevents impurities, primarily sulfate, from accumulating in the system. To limit the sulfate concentration in the membrane cell under the allowable tolerance, a minimal purge fraction is needed, which is determined based on the sensitivity study here.

The purge ratio (removed stream by the splitter divided by total stream entering the splitter) is varied from 0.2 to 1. The electrolyzer feed mass flow as well as its sulfate content with respect to the purge ratio is shown in Figure 5.

Figure 5 shows that the mass flow into the electrolyzer is decreasing with increasing purge ratio (horizontal axis). As shown, less purge and more recycling leads to higher system productivity. The recycling, however, is limited by the sulfate accumulation in the system. The impurities bromine and chlorate also accumulate, but at lower concentrations and further below tolerances than sulfate. As seen in Figure 5, a purge ratio between 0.3 and around 0.45 risks adverse effects (yellow zone) by high sulfate concentration (red line), and a ratio below 0.3 risks extreme impact by sulfate (red zone).

Based on this sensitivity study, a 0.5 purge ratio is selected for the system-level process, corresponding to a 1:1 ratio of recycle and purge streams. According to Figure 5, this purge ensures an electrolyzer feed sulfate concentration of about 3 g/L Na_2SO_4 (in the green zone) which maximizes cell performance while preventing possible adverse effects of sulfate accumulation.

OPERATION COSTS

With the energy consumption and chemical dosage obtained from the process model, the operational cost (OPEX) of the proposed system can be estimated. The calculations are summarized in Table 2.

Evidently, energy costs are dominant in the OPEX of the whole process. The membrane electrolyzer, as the primary energy consumer, contributes almost two thirds of the total operation costs. Concentration components ED, evaporator or MVC also has significant energy costs. Nevertheless, if the desalination plant is co-located with a power-plant (this is not uncommon), low grade heat could potentially be diverted to help lower the concentration cost.

Besides operating costs, the capital expenditure (CAPEX) also plays a dominant role in such a long-chain process. However, its estimation is highly site-specific, depending on several economic and other factors, and thus having very limited accuracy in a general case. We will not further focus on it but point out that it could be a direction for further studies.

COMPARISON OF THE PROCESS CHAIN WITH SIMILAR PROCESSES

In this section, our model for the process chain is compared against other existing models and the improvements and suggestions for future design are noted.

COMPARISON WITH STANDARD CHLOR-ALKALI

The major difference of the proposed process from the standard chlor-alkali industry lies in the feed stream. The feedstock in chlor-alkali industry is usually highly pure rock salt which requires no concentration step and fewer purification steps. As shown in Table 2, the pretreatment steps (NF, ED, MVC, chemical softening) in the brine-to-caustic process would cost around 0.0588 $ per kilogram caustic soda produced. If caustic soda were produced in excess of the brine-to-caustic needed internally at the RO plant (i.e., to generate extra revenue), this pretreatment cost should be compared with local rock salts (including the availability of rock salts locally, and the cost and quality of available salts) to decide whether it is economically feasible to produce excess saturated NaCl solution from RO brine.

COMPARISON WITH MELIAN-MARTEL[37]

In Melian-Martel's model of caustic production from RO brine, instead of controlling the sulfate concentration in the system by purging, barium is used to precipitate sulfate salts. Melian-Martel et al.

proposed the following process: Softening-MEE-IX-Electrolysis, where MEE is multi-effect-evaporation. The depleted brine from the electrolyzer is recycled after a dechlorination process. Additionally, they have calculated flows and concentrations in each stage.

While the final objective of their study is similar to ours, our process has the following differences/ improvements:

- Removal of sulfate: In our process, nanofiltration is used to reduce sulfate along with a brine purge, instead of using toxic and expensive barium salts. The sulfate concentration does not need to be lowered to the level of chemical precipitation as membrane cells are somewhat tolerant (purity requirements given in the section "Modeling details").
- Method of concentration: Melian-Martel used multi-effect evaporation (MEE) as a single-step concentration while we used ED as primary step and evaporation/MVC as final step. This saves energy.
- NaCl concentration: Melian-Martel's system concentrates the NaCl to 36 wt% in the MEE, and then dilutes it to 30.6 wt% for input to the membrane electrolyzer. In our system, maximal brine concentration is between 26 and 27 wt%. We suggest that high NaCl over-saturation (> 27 wt%) should be avoided as the precipitation of NaCl crystals may cause scaling in evaporators and pipes.

Overall, our process is technically more feasible due to the absence of oversaturated brines. Brine purging to remove sulfate is also easy to operate and reduces chemical treatment costs.

COMPARISON WITH GARRIGA[36]

The primary difference between the process chain suggested by Garriga and the present work is the addition of brine recycling. Garriga's process chain is NF-ED-Saturation-Softening-IX-Electrolysis.

Saturation is achieved by adding solid NaCl, as in the chlor-alkali industry. However, as salt is not presumed to be available as feedstock, the present process uses evaporation/MVC instead. Our process also has higher productivity and lower effluent volume due to the recycling of depleted brine.

ADVANTAGES, BEST-USE CASE, AND CHALLENGE OF THE PROCESS

Overall, the brine-to-caustic process investigated has the following advantages:

- Reduction of effluent from the RO facility:

  Overall, this process can reduce up to 29% of the RO facility effluent. The effluents of the process (see Figure 1) are the NF retentate (rate of 12.20 t/h) and the brine purge of (0.26 t/h) which in Figure 1 are the green box right next to RO bring inlet and the green arrow coming out of the teal box of dechlorination. The effluents have a higher concentration than the RO brine and can possibly be further concentrated in zero-liquid discharge processes, such as evaporation ponds.
- Reusing ED diluate:

  The ED step not only concentrates the brine, but also can improve the production of pure water thus reducing pure water costs as well. The ED diluate can be fed back to SWRO for increased recovery, since the diluate’s concentration of 3.5 wt% matches regular seawater. As this stream amounts for 26.2% of the RO brine, the actual water recovery of a regular RO plant (50%) would increase to 57.5%. Additionally, since this recycle stream comes from the RO brine, it does not require the costly extra pretreatment in the SWRO system which is necessary for fresh seawater.
- Avoiding of concentration-dilution cycle:

The proposed process avoids the steps of NaCl and NaOH concentration, transportation and dilution that are standard in chlor-alkali industry and desalination plants.

In standard chlor-alkali systems, solid salt is used as the feedstock and mostly originates from energy intensive evaporation and crystallization of an NaCl solution. Yet no energy is recovered when the salt is transported to a chlor-alkali facility and dissolved, resulting a loss of about 2.58 kWh heat per kg NaOH produced.

In RO plants, 50 wt% NaOH solution is typically obtained from chlor-alkali facilities and diluted for internal use. However, the 50 wt% solution is produced by evaporating the 30-35 wt% caustic soda from the electrolyzer.[28] This fraction of energy input (about 0.70 kWh heat/kg NaOH) is wasted by dilution.

- Potential revenue from side products:

The side products of the chlor-alkali process, H_2 and Cl_2, can generate substantial revenue. First, for every kilogram of caustic soda produced, 27.6 grams of hydrogen with a heat value of 0.92 kWh is co-produced. This heat could be directly applied in the evaporation step. Second, a relatively large amount of chlorine is produced, namely 0.87 kg per kg NaOH. Assuming a price of 250 \$/t[61] for chlorine, the potential revenue amounts to 0.22 \$/kg NaOH, nearly covering the operation costs listed in Table 2. It is crucial to mention, however, that the chlorine obtained through this process is a crude product (contains O_2, H_2O, possibly N_2 and CO_2) that can either be sold for a low price or has to be purified and liquefied yielding additional operation and capital costs.

Additionally, besides H_2 and Cl_2, it is also possible to produce more valuable side products on site, such as sodium hypochlorite, a typical bleaching chemical that is produced from NaOH and Cl_2.

- Reduction of transportation costs:

  The onsite production eliminates the transportation costs of NaOH for internal usage in SWRO plants.

  Additionally, as water is produced in RO facility as well as in the evaporator/MVC component of the brine-to-caustic system, the transportation costs of deionized water for the membrane electrolyzer (see Figure 1) can be saved.

The best-use case of the proposed brine-to-caustic process would be an SWRO desalination plant, satisfying some of the following points:

- Locations with scarce or expensive rock salt resources, corresponding to high price for standard chlor-alkali feedstock, and therefore making the brine-to-caustic process economically feasible not only for internal usage, but also for producing extra NaOH and Cl_2 for revenue.
- Remote desalination plants which are far from the nearest chlor-alkali facility, causing high transportation costs.
- High restrictions of boron content in the freshwater leading to high internal caustic usage.
- Limitations for RO brine discharge or legal benefits for low-impact discharge methods.
- Possible co-existing power plants that can supply waste heat for concentration processes.
- Possible co-existing chemical plants that can utilize the produced chlorine and excess NaOH.

Nevertheless, several challenges related to the process remain, for example the required know-how for each component in such an integrated process, as well as operation and control issues, especially during start-up and shut-down.

ENVIRONMENTAL IMPLICATIONS

The energy consumption and environmental impact of desalinated water production has become a major concern, especially due to the relative energy demands and required disposal of concentrated brine. The brine is usually discharged as wastewater, which can create a local imbalance in the ocean's salinity with negative impacts on marine ecosystems. Additionally, the treatment of water requires the use of caustic soda, of which the production and transportation contributes indirectly to the energy consumption of water production.[62]

In this study, a recovery process for creating caustic soda from desalination brine has been developed focusing on purification requirements and energy efficiency.

The present research not only develops a feasible process to produce caustic soda on-site at seawater desalination plants, but also explores the productivity, the energy use of the overall process, and the thermodynamic performance of the individual components. This process, as proposed at small-scale, can produce hundreds of metric tons of NaOH (a dry equivalent) per year, an amount that would fulfill the caustic soda needs of a typical, large-scale SWRO plant.[38] Moreover, if our NaOH recovery process was used on all the brine from a large-scale SWRO plant (about 10,000 kt/year), over 35,000 t caustic could be produced for commercial sale. The excess caustic production could be economically attractive, especially for desalination plants in remote locations, or with expensive local salt resources. Additionally, desalination plants using this process for the brine could increase typical water recovery from 50% to around 58%, reduce brine disposal volumes by 29%, save on pretreatment costs of feed water, and thus lower the normalized cost of freshwater. Furthermore, our process has a potential to reduce transportation, disposal costs, and emissions involved in brine disposal in other desalination applications that require zero liquid discharge.

ACKNOWLEDGEMENTS

The authors of this work gratefully acknowledge sponsorship by Cadagua, a Ferrovial subsidiary, through the MIT Energy Initiative. Aspen Plus from AspenTech, Inc. is used in this research. The authors also wish to thank Kishor G. Nayar for his suggestions on electrodialysis as well as Alicia Gómez González and Luis Alberto Letona Cabrida at Cadagua for providing important input parameters and giving practical insights.

CONTENTS OF SUPPORTING INFORMATION

- Brief introduction of modeling in Aspen Plus
- Modeling details of the membrane electrolyzer, validation and parametric study of the model
- Modeling details of the pre- and post-treatment components in the brine-to-caustic process chain
- Summary of mass flow, temperature and concentration at each stage of the process
- Brief introduction of least work analysis

NOMENCLATURE

Roman Symbols

f	-	Water transport number
F	C/mol	Faraday's constant (96,485 C/mol)
I	A	Electric current

$\dot{n}$	kmol/h	Molar flow
$\dot{Q}$	kW	Heat flow
T	°C	Temperature
U	V	Voltage
$\dot{W}$	kW	Work flow

Greek Symbols

η	-	Cathode current efficiency
η_{ED}	-	Current utilization factor in electrodialysis
η_{II}	-	Second law efficiency
ξ	-	Chlorine current (anode current) efficiency
ξ^{P}	-	Process chlorine efficiency

Subscripts

∞	Ambient
cell	Electrolyzer cell
least	Least (work)
Q	Heat source

Abbreviations

ED	Electrodialysis
ENRTL	Electrolyte- Non-random-two-liquid
IX	Ion-exchange
MEE	Multi-effect evaporation
MVC	Mechanical vapor compression
NF	Nanofiltration
ppb	Parts per billion (µg/kg)
ppm	Parts per million (mg/kg)
RK	Redlich-Kwong (equation of state)
RO	Reverse osmosis
SWRO	Seawater reverse osmosis
ZDL	Zero liquid discharge

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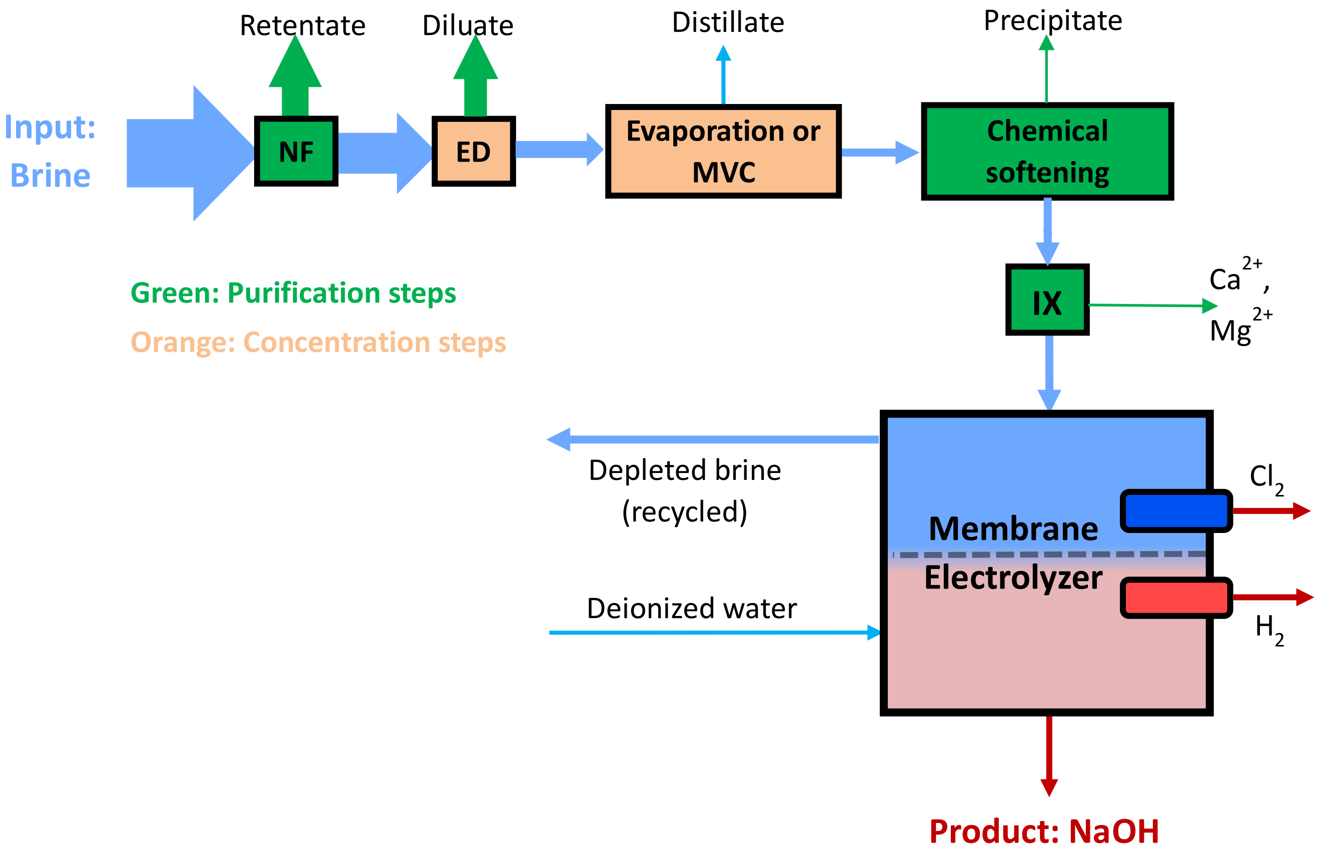
TOC figure


Retentate
Diluate
Distillate
Precipitate
Input: Brine
NF
ED
Evaporation or MVC
Chemical softening
Green: Purification steps
Orange: Concentration steps
IX
Ca^{2+}, Mg^{2+}
Depleted brine (recycled)
Deionized water
Membrane Electrolyzer
Cl_2
H_2
Product: NaOH

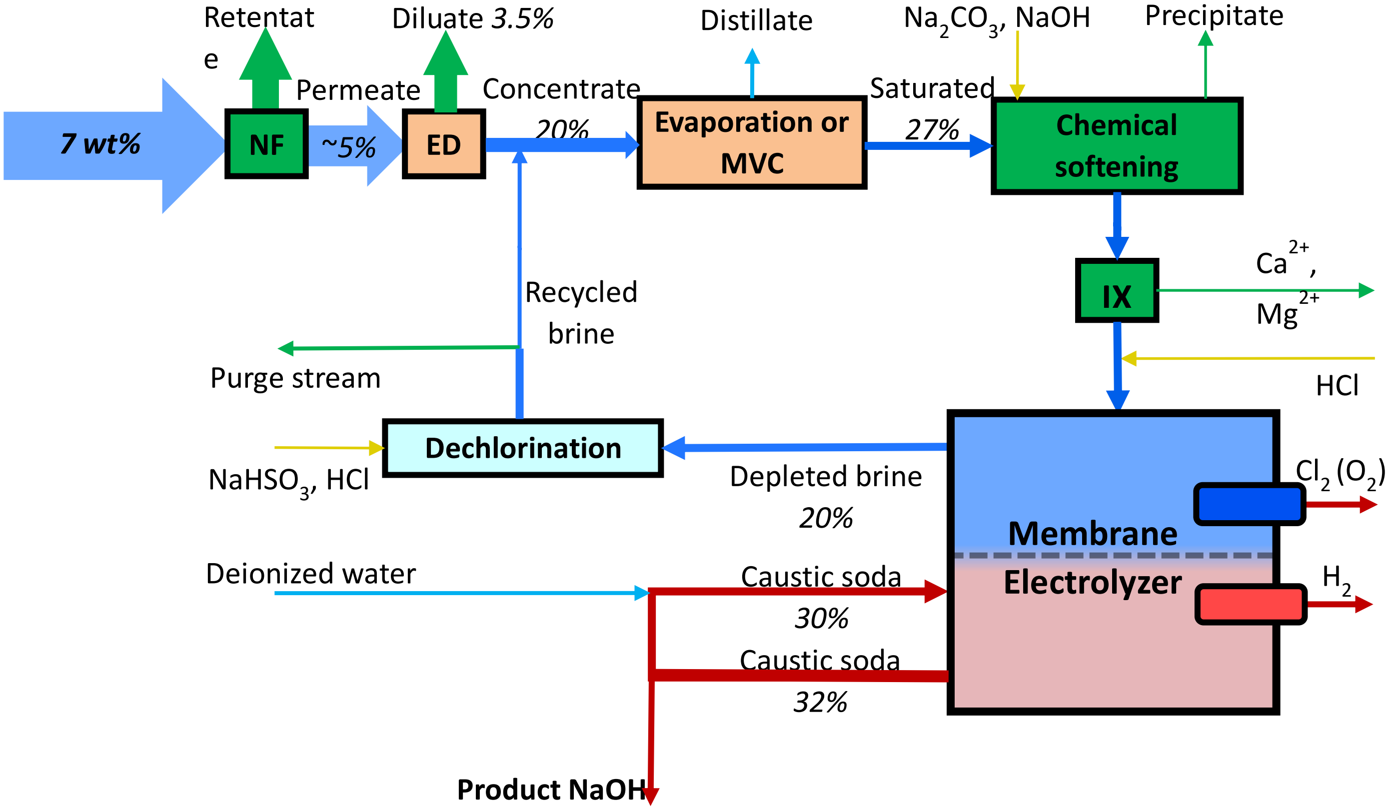


Figure 1. Brine to NaOH system block flow diagram for this study. Successive components purify (green) or concentrate (orange) the feed to reach suitable input conditions for a membrane electrolyzer. Typical brine and caustic concentrations are shown (percentage given as wt% solute). Color key of streams: Dark blue = brine streams; light blue = water; red = product; yellow = chemical dosage; green = effluent. Width of arrows indicates the mass flows. Starting from the inlet (left to right), the successive process includes nanofiltration (NF), electrodialysis (ED), evaporation or mechanical vapor compression (MVC), chemical softening, and ion-exchange (IX) as pretreatment components; the last step is the membrane electrolyzer as the NaOH production unit, with dechlorination as a post-treatment step. Components are chosen for purification capabilities (by concentration) and energy efficiency for concentration steps. Membrane electrolysis produce the primary product (NaOH) as well as the gases Cl_2 and H_2 at the electrodes.

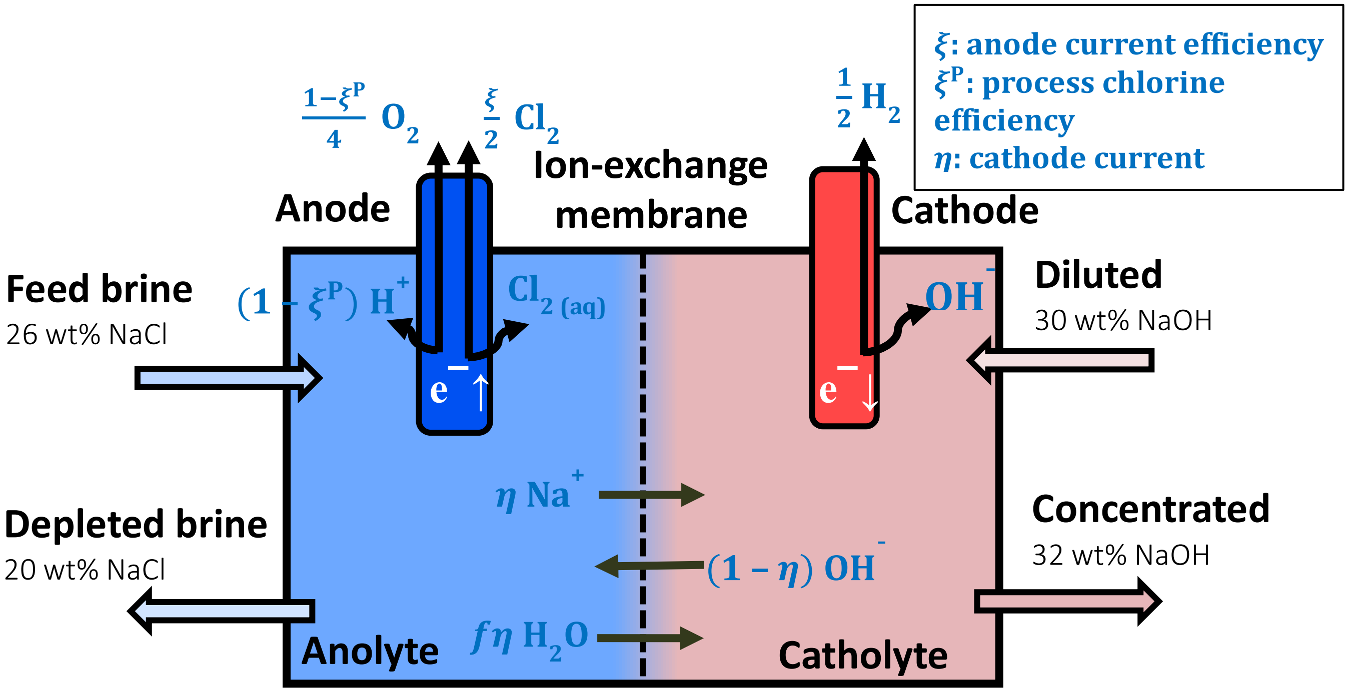


Figure 2. Schematic diagram of a typical cell for the chlor-alkali process, containing an ion-exchange membrane as well as anode and cathode for the reaction. The ion-exchange membrane separates the anode (left, blue) and the cathode chamber (right, red). Black arrows in the figure show species transported through the membrane and generated at the electrodes. Molar amount of species (blue formulas) are based on 1 mole of electrons (1 Faraday) consumed by the electrolyzer.

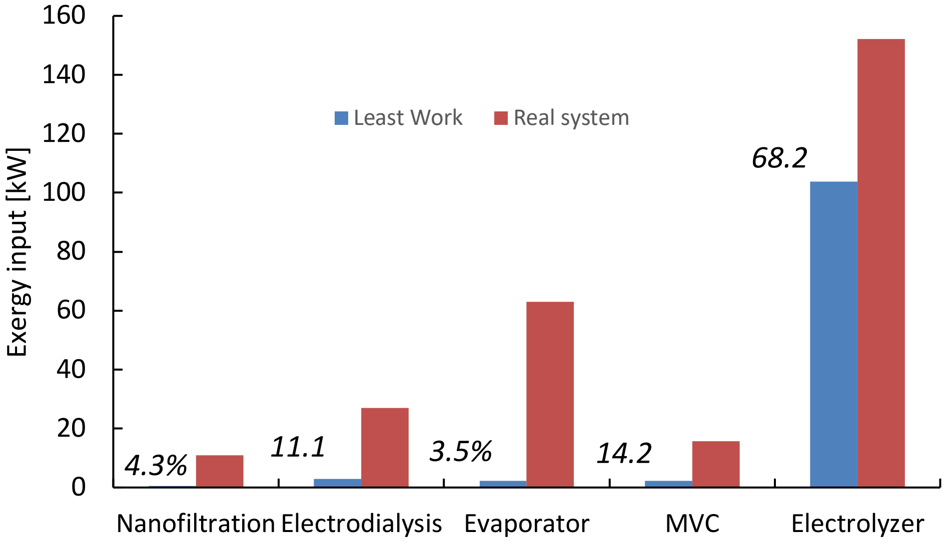


Figure 3. Least work compared to total consumed exergy (denominator in equation (2)) in the nanofiltration, electrodialysis, evaporation, MVC, and electrolyzer components. Percentages given are second law efficiencies (least work divided by actual exergy consumption).

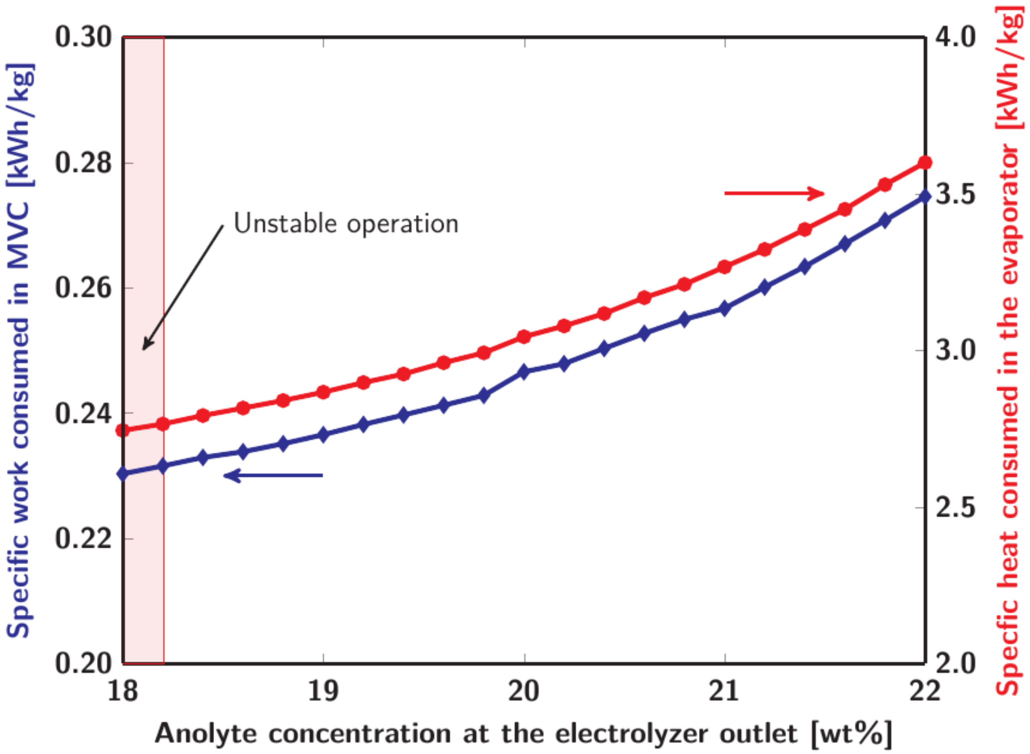


Figure 4. Evaporator (right, red) and MVC (left, blue) energy consumption normalized by the caustic production amount (as 32 wt% solution) with respect to the anolyte outlet concentration of the electrolyzer. A stable operation of the membrane electrolyzer is no longer feasible with anolyte concentration lower than 18.2 wt% (red zone).

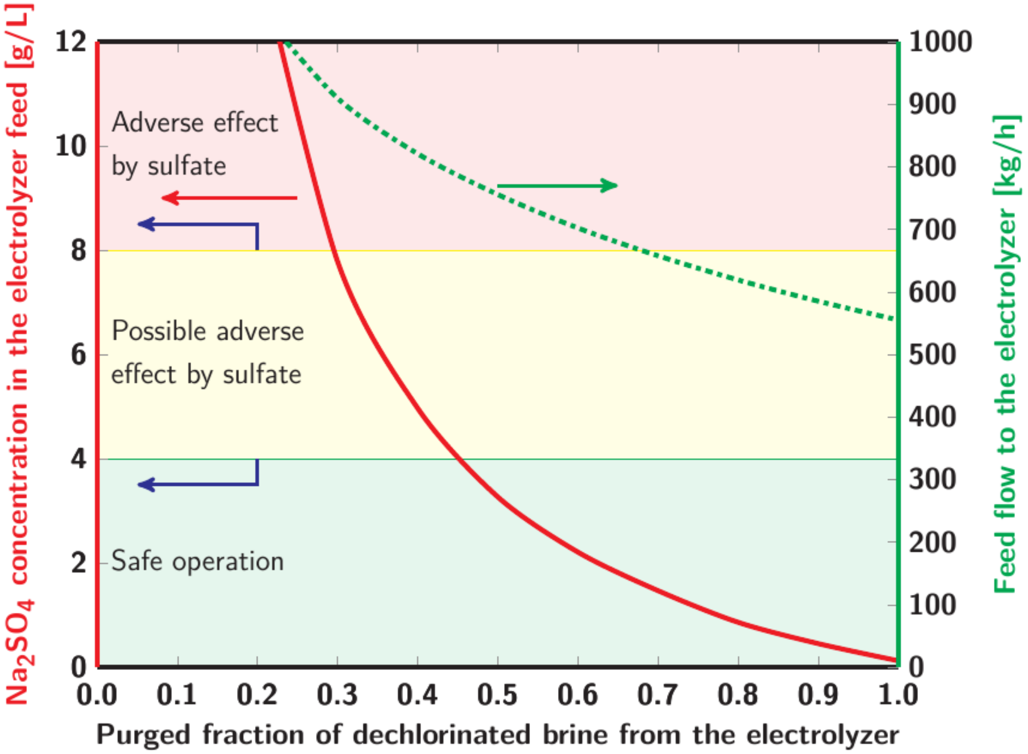


Figure 5. Impact of depleted brine purge on brine flow into electrolyzer and sulfate accumulation in the cell. Red and yellow zones indicate that the sulfate concentration exceeds tolerance in most membrane cells (> 8 g/L Na_2SO_4), or some membrane cells (> 4 g/L Na_2SO_4), respectively.[28,31,32] Green zone is free of adverse effects of sulfate.

Table 1. Selected modeling parameters and their values of the final system-level process.

Component	*Parameter*	*Value*	*Unit*	*Source/Rationale*
Feed brine	Temperature	25	°C	Ambient
	Mass fraction H_2O	91.87	%	Boundary condition.
	Mass fraction NaCl	6.39	%	Corresponds to 0.69 g/L Ca^{2+}, 2.2 g/L Mg^{2+}, 5.3 g/L SO_4^{2-}, 85 mg/L Br^- (based on density of 1059 kg/m^3 calculated by Aspen).
	Mass fraction $CaCl_2$	0.18	%	
	Mass fraction $MgCl_2$	0.81	%	
	Mass fraction Na_2SO_4	0.74	%	
	Mass fraction NaBr	0.01	%	

				2.75 wt% as Na$^+$ is the stoichiometric amount of typical 7.0 wt% SWRO brine
Nanofiltration	Temperature	26	°C	Isothermal, temperature after pumping is 25.6 °C
	Pressure feed	20	bar	Typical value for high-salinity feeds[36,51,52]
	Water recovery	30.3	%	ROSA Simulation[53,54]: Two-stage system with six NF270-400 elements per stage, see SI "Nanofiltration"
	Rejection of Cl$^-$	16.1	%	
	Rejection of SO$_4^{2-}$	95.7	%	
	Rejection of Ca^{2+}	38.3	%	
	Rejection of Mg^{2+}	40.1	%	
	Rejection of Br$^-$	16.1	%	Assumed same as Cl$^-$
	Pump efficiency	80	%	Estimation
Eletrodialysis (C: concentrate, D: diluate)	Temperature	26	°C	Assumed isothermal
	Outlet concentration C	20	wt%	Industrial upper limit[46]
	Outlet concentration D	3.5	wt%	Can be fed back to RO plant
Evaporator	Temperature	108	°C	Brine temperature at 1 bar with saturated NaCl
	Brine concentration outlet	27	wt%	Ensure saturated brine for the electrolyzer
Chemical Softening	Temperature	60	°C	High enough to speed up the precipitation process (source IPPC, cited by Garriga[36] same as ion exchange
Ion exchange	Temperature	60	°C	Recommended temperature[55]
Electrolyzer	Temperature	88	°C	Reference plant[28]
	Pressure anolyte	1.09	bar	Reference plant[28]
	Pressure catholyte	1.05	bar	Reference plant[28]
	Feed brine pH value	3	-	See SI "Anode and cathode current efficiencies in electrolyzer"
	Product NaOH concentration	32	wt%	Reference plant[28]
	Recycle NaOH concentration	30.3	wt%	Reference plant[28]
	Cathode current efficiency	94	%	Reference plant[28]
	Anode current efficiency	96	%	Estimation
	Water transport number	4.25	-	Reference plant[28]
	Anolyte outlet concentration	19	wt%	See section "Anolyte outlet concentration"

	Voltage of the electrolyzer	3.2	V	Reference plant[28]
Purge splitter	Purge ratio	0.5	-	See section “Purge ratio”
Dechlorination	Temperature	88	°C	Adiabatic mixing

Table 2. Estimated operation expenditures of the purposed system. Cost normalized by the caustic production of 64.8 kg/h.

Component	Consumption	Cost per unit	Cost per produced NaOH
NF	10.9 kW electricity	0.0695 \$/kWh[59]	0.0117 \$/kg
ED	26.8 kW electricity	0.0695 \$/kWh[59]	0.0288 \$/kg
Electrolyzer	152.1 kW electricity	0.0695 \$/kWh[59]	0.1631 \$/kg
Evaporator/ MVC	190.8 kW heat / 15.8 kW electricity	0.0102 \$/kWh (based on natural gas price[60] / 0.0695 \$/kWh[59]	0.0301 \$/kg 0.0169 \$/kg
Chemical softening	16.2 kg/h Na_2CO_3 (3.6 wt%)	0.165 \$/kg dry[61]	0.0014 \$/kg
Ion-exchange	0.154 kg/h HCl (6 wt%)	0.243 \$/kg (dry base)[61]	<0.0001 \$/kg
Acidifier	1.356 kg/h HCl (37 wt%)	0.243 \$/kg (dry base)[61]	0.0018 \$/kg
Dechlorination	4.321 kg/h $NaHSO_3$ (38 wt%)	0.529 \$/kg dry[61]	0.0130 \$/kg
TOTAL			0.2501 \$/kg (Evaporator) 0.2369 \$/kg (MVC)