

Utilization of Desalination Brine for Sodium Hydroxide Production: Technologies, Engineering Principles, Recovery Limits, and Future Directions

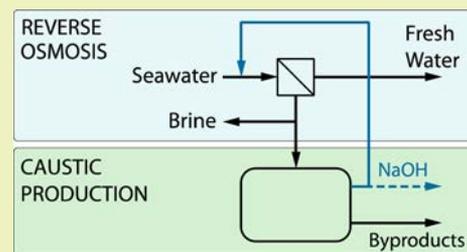
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ABSTRACT: As global desalination capacity continues its rapid growth, the impetus for reducing the adverse environmental impacts of brine discharge grows concurrently. Although modern brine outfall designs have significantly limited such impacts, they are costly. Recovering valuable components and chemical derivatives from brine has potential to resolve both environmental and economic concerns. In this article, methods for producing sodium hydroxide (“caustic”) from seawater reverse osmosis (SWRO) brine for internal reuse, which typically involve brine purification, brine concentration, and sodium chloride electrolysis, are reviewed. Because process energy consumption drives process cost and caustic purity determines product usability in drinking water systems, reviewed technologies are benchmarked against thermodynamic minimum energy consumption and maximum (stoichiometric) NaOH production rates. After individual reviews of brine purification, concentration, and electrolysis technologies, five existing facilities for caustic production from seawater and seawater concentrates are discussed. Bipolar membrane electrodialysis appears to have the best potential to meet the technoeconomic requirements of small-scale caustic production from SWRO brine. Finally, future research and demonstration needs, to bring the technology to commercial feasibility, are identified.

KEYWORDS: NaOH, Caustic, Reverse osmosis, Bipolar membrane electrodialysis, Chlor-alkali, Electrolysis, Waste-to-resource, Circular economy



INTRODUCTION

Environmental and economic factors have long motivated interest in reducing the amount of brine discharged back into the ocean by seawater desalination plants. Modern designs for brine outfalls can limit adverse environmental impacts to “tens of meters” from the discharge source^{1,2} but are high cost.³ An emerging class of solutions, broadly titled *waste-to-resource*, aim to reduce brine discharge by transforming it into useful compounds.^{4–7}

Many previous such studies focus on recovering salts, of which the largest by mass is sodium chloride. But in many countries, NaCl exists in abundant, cheap supply as rock salt or brine, meaning any competing source must be extremely low cost. [The US Geological Survey reports average US rock salt and brine prices ranging from 38–50 USD/ton and 8–9 USD/ton, respectively, from 2011–2015.⁸] Its chemical derivatives, primarily soda ash, caustic soda (“caustic”), and chlorine, however, may be much higher value. Nearly 30% of NaCl sold in the US⁸ is used as a feedstock in the chlor-alkali process to manufacture the most common of these at large scale: NaOH and Cl₂. Also, NaOH is frequently used within the desalination plant itself.

Consequently, producing NaOH from seawater reverse osmosis (SWRO) brine for reuse within the SWRO facility

has the potential to benefit environment and plant economics. By replacing NaOH manufactured off-site using chlor-alkali by an on-site, lower-energy process (e.g., one producing HCl as a byproduct instead of Cl₂), the environmental and economic footprints of NaOH generation and transport are reduced. By diverting a portion of the brine discharge, less salt flows into the ocean, resulting in lower salt concentrations around brine discharge ports, which lessen the plant’s impact on marine life. Further, since both benefits scale with the amount of NaOH produced, any other nearby consumers of the NaOH produced would serve to increase the positive environmental and economic impacts of this technology.

In this article, we review possible methods for producing NaOH from SWRO brine. We focus on meeting typical concentration and purity requirements for internal reuse and process energy consumption, which together largely determine technoeconomic feasibility. Although a chlorine-containing byproduct is necessarily produced with the NaOH, the NaOH demand is the process driver, and so NaOH is the focal point of this article. (Many chlorine-based byproducts also

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have potential use within the desalination plant, for example, HCl for cleaning; CaOCl_2 , Cl_2 , or NaOCl for chlorination.^{9,10} The article begins with an overview of the uses, manufacture, and historical price of caustic soda and a summary of typical needs in SWRO facilities. Then, we outline the high-level process of making NaOH from SWRO brine, including minimum energy requirements. The two subsequent sections review available technologies for NaOH production, brine purification, and brine concentration. The article concludes with a review of existing plants that manufacture NaOH from seawater or desalination brine and recommendations for further study.

Caustic Soda: Uses, Commercial Production, and Market Overview. Caustic soda has myriad uses both internal and external to the desalination plant. Internally, treating seawater feed with caustic soda increases the pH. At higher pH, several compounds are better rejected by the RO membrane. Around pH 9, the better-rejected borate anion $\text{B}(\text{OH})_4^-$ supplants boric acid as the dominant aqueous boron species.¹¹ The dissolved silica system behaves similarly, with the dominant $\text{SiO}(\text{OH})_3^-$ and $\text{SiO}_2(\text{OH})_2^{2-}$ species above pH 9 yielding better silica rejection,¹² and above pH 8, dissolved inorganic carbon exists as bicarbonate and free carbonate, which are better rejected than aqueous carbon dioxide.¹³ Evidence also shows reduced organic fouling at high pH.¹⁴ Finally, caustic soda is an ingredient in cleaning solutions to remove organic, biological, and organic/inorganic colloidal foulants and silica scale.¹⁵

For internal reuse, caustic soda purity requirements are moderate. Membrane manufacturers manuals for reverse osmosis¹⁶ rate technical grade as sufficient purity for membrane and system compatibility. However, more stringent standards may exist at national or subnational levels, depending on the application. For drinking water reverse osmosis, for example, EN 896¹⁷ in the EU and NSF/ANSI 60¹⁸ in the US are relevant.

In addition to its use in controlling pH and neutralizing acids, caustic soda is used as a reagent in the production of many chemicals. About 59% of NaOH in the EU and North America is used in the pulp and paper, inorganic, and organic chemical industries.¹⁹ Soaps and detergent manufacture also account for significant demand. For external reuse, quality requirements are application specific, and some commercially produced caustic soda is of insufficient purity for certain industries. For example, caustic soda produced using the diaphragm process is not suitable for manufacturing viscose, also known as rayon.^{20,21}

Industrial production of caustic soda is massive. Global manufacture exceeded 59 million tons in 2004,¹⁹ with significant growth in demand and capacity expected in Asia.²⁰ Production is also scalable, with plant capacities ranging from about 4.4 kt/yr (Kapachim, Inofita Viotias, Greece) to 1744 kt/yr (Dow, Stade, Germany) in the EU²² and about 2 to 3333 kt/yr (Olin, Freeport, TX) in the US^{20,23} on a dry basis. [Estimated from chlorine capacity at 1.1 kt NaOH/kt chlorine,¹⁸ which is slightly less than stoichiometric.] On the small end, ThyssenKrupp Uhde GmbH offers standardized skid-mounted plants at up to 17 kt/yr, and AVS Technology AG offers plants as small as 1.1 t/d.

About 99.5% of global caustic soda production is by the chlor-alkali process.²⁴ Briefly, the process produces caustic soda and chlorine gas in equimolar amounts by electrolysis of aqueous sodium chloride. Direct synthesis of process products can also produce hydrochloric acid, though less than 10% of

HCl is manufactured this way.²⁵ (Technical aspects of the chlor-alkali process and other methods are discussed in-depth below.) Three variants of the process exist in widespread commercial use, generally distinguished by how catholyte and anolyte are separated. The variants are known as the membrane, diaphragm, and mercury processes. The membrane process dominates modern installed capacity owing to fewer environmental concerns—containing neither mercury nor asbestos-based diaphragms—and lower energy consumption. The installed capacity in the EU in 2014 is sorted by type in Figure 1. Mercury process capacity dropped by 56% between 2002 and 2014 and continues to do so, by both decommissioning and retrofit.²⁶

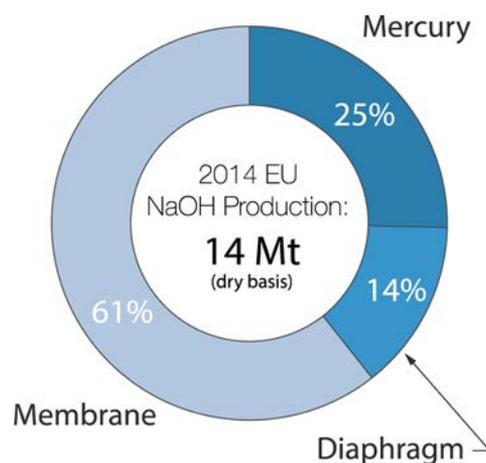


Figure 1. Total estimated EU-wide caustic soda production in 2014, segregated by process type, based on EuroChlor plant data.²²

Constrained by the chemistry of the chlor-alkali process, most caustic soda is coproduced with chlorine in equimolar amounts, yielding a near perfectly correlated supply. However, demand for caustic soda and chlorine is not perfectly correlated. This mismatch can lead to large changes in price.²⁷ As seen in the EU data shown in Figure 2, between January 2005 and

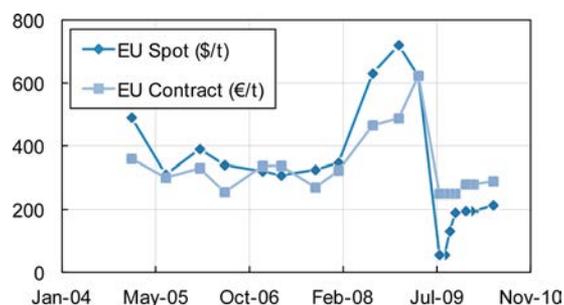


Figure 2. Prices for caustic soda in the EU ranged from 55–720 USD/t on the spot market between 2005 and 2009 (Data source: Chemical Week Price Report).

November 2009, caustic soda prices in the EU soared as high as 720 USD/t before dropping to 55 USD/t. Contract prices were more stable, ranging between 215 and 622 EUR/t.

Operational costs are driven largely by energy cost. In a recent investor report, Olin²⁸ notes that “electricity is 80% of chlor-alkali variable production cost”. Lindley²⁹ reports power costs between 32% and 45% of total direct costs in the EU. A U.S. EPA report³⁰ shows energy as 32% of total production

costs, based on industrial census data. Without plant-specific cost and regional energy price data, it is difficult to narrow these ranges, but the significance of energy cost is apparent even as a component of price: at 0.075 EUR/kWh, energy accounts for about 20–48% of total price for caustic soda sold at 200–400 EUR/t and typical energy consumption (Figure 2). Also, the significance of energy cost is only compounded by energy price volatility, which itself can add additional costs, for example, in the form of hedges or higher contract pricing.

Overview of Process Requirements, and Boundary Conditions. Caustic soda is used in SWRO plants to increase boron rejection and as a part of dechlorination. NaOH is typically purchased as a 50% (w/w) aqueous solution, the typical commercial concentration, and then diluted to between 3–26% (w/w) for dosing. The amount used varies significantly between plants, typically in the tens to hundreds of tons per year on a dry basis. Table 1 gives a summary of caustic usage

Table 1. Summary of Caustic Soda Usage and Available Brine Supply at Three Typical, Large-Scale SWRO Plants^a

Plant	1	2	3
NaOH Conc. Req'd. [%]	—	26.3	3.1
NaOH Use [t/yr, dry]	38	60	324
Brine Flow [$\times 10^6$ m ³ /yr]	39.81	10.38	31.76
Req'd Brine [t/yr]	792	1250	6750
% of Brine Flow	0.002%	0.01	0.02

^aNaOH usage is quoted on a dry basis. Brine density taken as 1.04 kg/L.

and brine availability at three plants where caustic soda could be directly produced from SWRO brine. Typical historical contract prices are approximately between 195 and 205 EUR/t (50% w/w solution).

Caustic soda purity requirements are dictated by site-specific regulations and/or standards. In the EU, for example, the standard EN 896¹⁷ is controlling. The standard contains quantitative purity requirements and methods for sampling. Major impurities, like NaCl, Na₂CO₃, and NaClO₃, have limits similar to their concentrations in commercial (diaphragm-grade) caustic soda. Relative to the mass of Na in typical seawater, no minor impurities—trace metals such as As, Cd, Pb—exceed EN 896 limits. However, Hg and Ni are within 1 order of magnitude of the limit. Since the concentration of trace metals varies, potentially significantly near a source, onsite testing should confirm that minor impurity limits are not exceeded.

■ PROCESS OVERVIEW AND LIMITS

In this section, we evaluate the process at high level to develop performance benchmarks for technologies reviewed in subsequent article sections. In particular, we discuss bounds for energy consumption and productivity, i.e., caustic soda production per unit feed.

A block diagram of the process is shown in Figure 3. A portion of the SWRO brine is redirected (state 1) where it is purified (Block 1) and then concentrated (Block 2). In the concentration process, additional valuable water is produced (state 2), offsetting the cost of the caustic recovery. As the brine is purified, some byproducts are removed (state 3). However, for these bounding estimates, we set the mass flow rate of this stream, \dot{m}_3 , to zero.

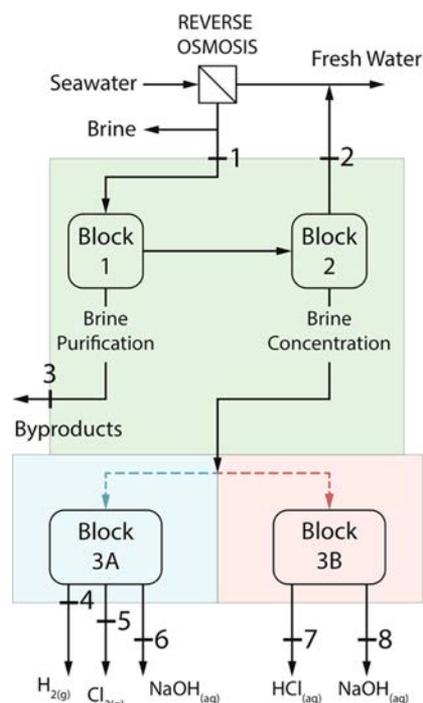


Figure 3. Process block diagram: a portion of the SWRO brine is redirected through brine purification and concentration steps, Blocks 1 and 2. In Variant A (green and blue areas), the purified brine is separated into hydrogen, chlorine, and caustic soda. In Variant B (green and red areas), the purified brine is separated into hydrochloric acid and caustic soda. In both variants, the chlorine-based byproducts have uses within the RO plant: chlorine as a disinfectant and hydrochloric acid as a membrane cleaning agent or as a regenerant for ion-exchange systems used in pretreatment.

We analyze two process pathways for the purified and concentrated brine. Variant A, shaded blue in Figure 3, is the standard chlor-alkali process: it consumes brine and produces hydrogen gas,⁴ chlorine gas,⁵ and NaOH.⁶ Variant B, shaded red, consumes brine and produces HCl⁷ and NaOH.⁸ Pathways for the chlorine-based byproducts will be plant-specific, but all can be used within the RO facility. For example, chlorine gas is a broadly used disinfectant, and HCl is used for RO membrane cleaning, regeneration of ion exchange systems in RO pretreatment trains, and even in combination with NaOH for stream-specific pH control.

Process Productivity. The following analysis computes an upper bound on the amount of caustic and other products produced by assuming all sodium in the redirected brine is converted to NaOH and all chlorine in the redirected brine becomes HCl.

Variant A: SWRO-Brine-Fed Chlor-Alkali. In variant A, chloride in the brine stream is oxidized to chlorine gas and protons from split water are reduced to produced hydrogen gas, leaving NaOH in the aqueous phase. By stoichiometry and mass conservation

$$\frac{\dot{m}_6}{\dot{m}_1} = \frac{w_{\text{NaCl},1} M_{\text{NaOH}}}{M_{\text{NaCl}} w_{\text{NaOH},6}} \quad (1)$$

$$\frac{\dot{m}_5}{\dot{m}_1} = \frac{w_{\text{NaCl},1} M_{\text{Cl}_2}}{M_{\text{NaCl}} 2w_{\text{Cl}_2,5}} \quad (2)$$

Consequently, 1 kg of a typical 7% w/w brine can produce up to 96 g of 50% w/w NaOH_(aq), 42 g of Cl_{2(g)}, and 1.2 g of H_{2(g)}.

Variant B: Brine Electrolysis. In Variant B, the purified brine is split into its acid and base components. Since we are interested in an upper bound on productivity, we prescribe all sodium in the redirected brine to be converted to caustic soda. Again, by mass conservation and stoichiometry:

$$\frac{\dot{m}_8}{\dot{m}_1} = \frac{w_{\text{NaCl},1} M_{\text{NaOH}}}{M_{\text{NaCl}} w_{\text{NaOH},8}} \quad (3)$$

$$\frac{\dot{m}_7}{\dot{m}_1} = \frac{w_{\text{NaCl},1} M_{\text{HCl}}}{M_{\text{NaCl}} w_{\text{HCl},7}} \quad (4)$$

Finally, we evaluate the additional water produced. By mass conservation, all water not remaining in the final acid and caustic streams must end up as product, i.e., $\dot{m}_2 = \dot{m}_1 - \dot{m}_8 - \dot{m}_7$. Normalizing by the incoming brine flow rate and substituting in eqs 4 and 3 yields the final expression for recovered water as a function of the desired caustic and HCl purity:

$$\frac{\dot{m}_2}{\dot{m}_1} = 1 - \frac{w_{\text{NaCl},1} M_{\text{NaOH}}}{M_{\text{NaCl}} w_{\text{NaOH},8}} - \frac{w_{\text{NaCl},1} M_{\text{HCl}}}{M_{\text{NaCl}} w_{\text{HCl},7}} \quad (5)$$

For a typical 7% brine and typical commercial concentrations of NaOH (50% w/w), we see that 96 g of NaOH_(aq) are produced per kg of brine, or about 48 g on a dry basis. At typical HCl concentrations (10% w/w), a maximum of about 437 g HCl_(aq) results per kg of brine, or about 44 g on a dry basis. Consequently, for each kg of brine, 467 g of additional pure water are recovered.

Because the amount of NaCl in the brine is so small, the productivity is also small. However, typical total NaOH use relative to brine flow rates is also small. In order to meet typical NaOH needs within SWRO plants (tens to hundreds of tons per year), between hundreds to thousands of t/yr of brine is required—well under a percent of a typical plant brine flow rate (Table 1). Consequently, any such retrofit for internal reuse will have little to no effect on the existing brine outfall, and the additional water produced will also be relatively minimal.

Least Work Analysis. Above, we sought to bound the amount of caustic that can be produced from SWRO brine. Since energy is such a large cost, we now seek to understand the energetic limits; that is, we evaluate the thermodynamic least work required to produce caustic and the other products of variants A and B from SWRO brine.

The nature and number of compounds to be removed during brine purification depends upon specific process requirements for Blocks 2, 3A, and 3B. The minimum energy will, therefore, also depend on those requirements. Since we are seeking a lower bound on energy consumption, we set the stream 3 mass flow rate to zero in the following analyses—in the bounding case, the best processes for Blocks 2, 3A, and 3B would require no brine purification.

For both Variant A and Variant B, we apply the First and Second Laws of Thermodynamics to the appropriate control volumes and find the minimum (i.e., reversible) work required for each process by setting the entropy generation term to zero, yielding the following expression (see Appendix A for a detailed development):

$$\dot{W}_{rev} = \sum_o \dot{G}_o - \sum_i \dot{G}_i \quad (6)$$

where \dot{G} is the flow rate of Gibbs energy, and the sums are across all outlet o and inlet i streams.

Variant A. The reversible work for Variant A (see Appendix A.1 for development), normalized per unit NaOH produced, is shown graphically in Figure 4 as a function of desired final

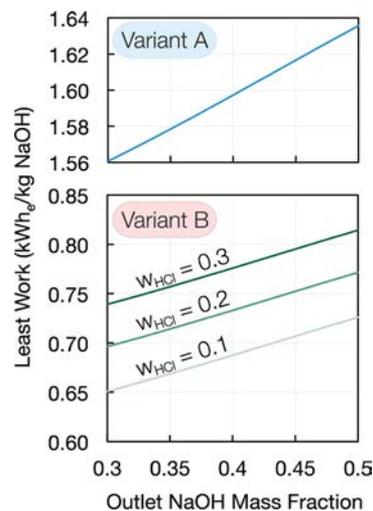


Figure 4. Least work of separation for the chlor-alkali process (Variant A) is more than twice that of direct acid–base production (Variant B) for typical outlet NaOH and HCl concentrations.

caustic soda concentration. At typical commercial caustic soda concentrations, 50% w/w, the minimum energy required is 1.64 kWh_e/kg NaOH. At a typical industrial electricity cost of 0.075 EUR/kWh, this corresponds to a minimum energy cost of 123 EUR/t NaOH.

At the same concentration, the portion of that energy required for brine concentration is 0.06 kWh_e/kg NaOH, or about 3.7 kWh_e/t H₂O. From a reversible perspective, there is no energetic benefit to producing a greater concentration of caustic soda than any individual SWRO plant requires, but the energy required for brine concentration is a small fraction (1.8%) of the overall least work. However, typical brine concentration systems may have efficiencies near 10–20%,³¹ meaning in actual systems brine concentration may consume 10–20% of overall energy costs.

If there is no chemical use for the hydrogen produced by Variant A, some energy can be recovered by combusting it or using it in a fuel cell. At best, in the reversible limit, a (Carnot) heat engine operating between the adiabatic flame temperature of H_{2(g)}, 2483 K, and a sink temperature of 298 K has a first law efficiency of 88%. The higher heating value of H_{2(g)} is 286 kJ/mol, so the maximum work we could recover is 252 kJ/mol H_{2(g)}. (In reality, the energy obtained would be considerably lower.) On a NaOH product mass basis, this equates to 0.875 kWh_e/kg NaOH—a considerable reduction on typical Variant A energy consumption values (1.56–1.64 kWh_e/kg NaOH, Figure 4).

Variant B. Figure 4 shows Variant B's minimum energy requirement as a function of the desired acid and base concentration, evaluated using eq 9 on a mass basis, i.e., divided by M_{NaOH} . For typical commercial concentrations, 50% w/w NaOH and 10% w/w HCl, the least work is 0.73 kWh_e/kg. At an electricity price of 0.075 EUR/kWh, this corresponds to 55

EUR/t NaOH. If Variant A and B irreversibilities are similar, Variant B is thus likely to have a lower energetic cost. In both variants, the energy required to oxidize Cl^- and electrolyze water dominate the energy required for feed and product concentration (see Appendix A).

Caustic Soda Concentration. In the preceding analyses, we have implicitly included the minimum energy cost of caustic soda concentration by specifying a variable outlet NaOH mass fraction. However, SWRO operators often do not require commercial (50% w/w) concentrations, and commercial processes generally do not produce 50% w/w caustic soda without a postproduction concentration step. Therefore, it is useful to break out this energy cost to identify potential savings and to benchmark existing caustic soda concentration processes.

As with the above analyses, we use a thermodynamic idealization to compute least work. The caustic soda enters the black-box concentrator (inset Figure 5) at a specified feed state

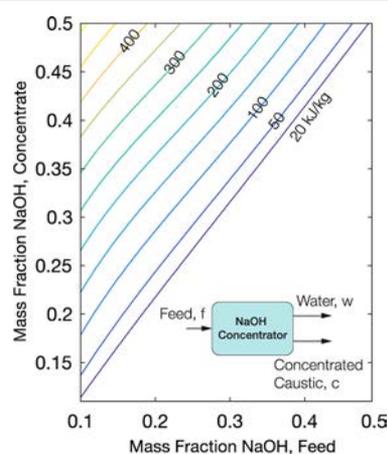


Figure 5. Least work for caustic soda concentration. Caustic soda enters the “black box” NaOH concentrator at a feed state f and pure water w is removed, resulting in the desired concentrate c . Depending on the mass fraction of NaOH in the feed and concentrate, the minimum energy required to concentrate can be up to 512 kJ/kg NaOH, or 0.14 kWh/kg NaOH.

f and pure water is removed, resulting in two product streams: the water w and the concentrate c . Results as energy consumption per kg of NaOH are given in Figure 5, which shows contours of least work for specified feed and concentrate NaOH mass fractions (see Appendix A for development). For a cell that produces 30% w/w NaOH and is concentrated to 50% w/w, the least work is about 270 kJ/kg NaOH, or 0.075 kWh_e/kg NaOH. At an electricity cost of 0.075 EUR/kWh, this equates to a minimum savings of about 5.63 EUR/t if caustic soda concentration is not employed.

Review of Available Technologies for NaOH Production. In this section, we review the available technologies for producing NaOH from NaCl streams. The primary foci are the chlor-alkali process, which is the commonest commercial method for NaOH manufacture, and bipolar membrane electrodialysis, which is a late-stage research technology. Some other methods for salt electrolysis are discussed in the subsection that follows.

Chlor-Alkali Process and Cell Overview. As discussed in the Introduction, the chlor-alkali process produces NaOH, hydrogen gas, and chlorine gas from an NaCl feed. Three main

variants exist: the membrane cell, diaphragm cell, and mercury processes. Because the mercury process is increasingly falling into disuse,²⁶ we only describe the membrane cell and diaphragm cell processes. We first discuss the electrolytic cell itself, then the post-treatment steps and typical purity levels, then the pretreatment requirements, and finally the energy requirements of the processes.

Diaphragm and Membrane Cells. The heart of both processes is the electrolytic cell, where NaCl electrolysis occurs. The membrane and diaphragm cells are shown schematically in Figure 6. In both processes, saturated NaCl (26% w/w) is fed to the cell, and chloride ions are oxidized at the anode according to the half-reaction

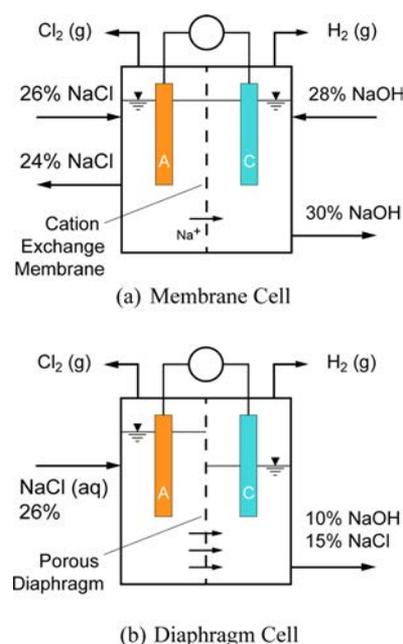
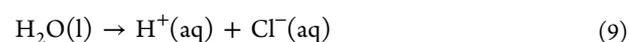


Figure 6. Schematic diagrams of the membrane and diaphragm cells: in both, a saturated NaCl solution is electrolyzed to produce chlorine and hydrogen gas. In the membrane cell, backflow of the catholyte is prevented by a cation-selective ion exchange membrane; in the diaphragm cell, NaCl a hydrostatic pressure difference drives solution from anode to cathode chamber.

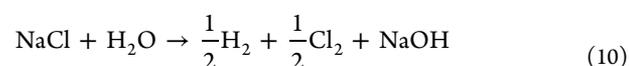
Hydrogen ions in the water are then depleted by reduction at the cathode according to



which then drives water electrolysis in the catholyte:



The overall reaction in both cells is thus



Saturated NaCl (26% w/w) is required to avoid oxygen evolution at the anode.

The two cells are distinguished by how the anolyte and catholyte are separated, which prevents product loss by backmixing of OH^- with chlorine to form hypochlorite. In the membrane cell, the oxidized chloride's sodium counterion

passes through an ion exchange membrane that selectively admits cations but rejects anions. The remaining, unreacted chloride is thus prevented from mixing with the catholyte and exits the cell with an equal number of sodium cations. This outlet stream is typically about 24% w/w NaCl and is recirculated. [Before it can be reblended, however, a dechlorination step is required. This dechlorination step removes chlorates produced at the anode.] On the cathode side, water from the aqueous NaOH feed (28% w/w) is split, the H⁺ is reduced, and OH⁻ remains. Together with the Na⁺ admitted by the membrane, this yields a net increase in NaOH concentration (to 30% w/w), which becomes the outlet stream. A portion of this outlet stream is recirculated and diluted with makeup water to become the 28% w/w feed stream.

In the diaphragm cell, a porous separator, the diaphragm, separates anolyte and catholyte. This separator is not charge selective, but it does provide a physical barrier. This physical barrier allows the anolyte to be maintained at a higher hydraulic pressure, causing a continuous convection of aqueous NaCl from the inlet, past the anode, through the pores, and into the cathode compartment. This continuous flow from anode to cathode compartment prevents backmixing of the catholyte. As the NaCl stream passes the anode, some chloride is oxidized. The remaining fraction of Na⁺ and Cl⁻ that passes through the diaphragm mixes with the hydroxyl ions in the cathode compartment to produce an electroneutral mixture of NaOH and NaCl.

Post-Treatment and Purity. In both cells, a number of post-treatment steps are required. The caustic soda produced by the membrane cell is typically very pure. Typically, only evaporation is performed postcell, usually two- to three-effect evaporation,¹⁹ in order to reach commercial concentrations. In diaphragm cells, the largest impurity is sodium chloride, which is removed by fractional crystallization. As the outlet caustic is evaporated, sodium chloride becomes less soluble and precipitates out of the solution. When the caustic soda is at 50% w/w, NaCl solubility is near 1% w/w, and so this amount remains in solution.¹⁹ Gas (chlorine and hydrogen) purity and postprocessing depend on the process and intended use.²¹

For typical SWRO applications, caustic soda concentrations lower than 50% w/w are acceptable. In the membrane cell, sufficiently pure caustic soda at lower concentration is available at the cell outlet. Using the membrane process, postcell concentration would therefore not be required. However, since the NaCl in the diaphragm product is a consequence of postcell evaporation, this step is required when using the diaphragm cell.

Some other impurities controlled by the EU caustic standards for drinking water applications¹⁷ are shown in Table 2. Relative to the EU standards, products from both the

Table 2. Both Membrane and Diaphragm Processes Produce Sufficient Purity Caustic Soda To Meet EU Drinking Water Standards^a

Impurity	Amount (g/kg NaOH)		
	Diaphragm		Membrane
	Unpurified	Purified	
NaCl	20	0.5	0.1
Na ₂ CO ₃	2	2	0.8
NaClO ₃	2	0.02	0.02

^aData adapted from ref 21.

diaphragm and membrane processes are sufficiently pure. However, caustic soda purity from the diaphragm cell is more dependent upon feed brine purity, since brine passes directly through the diaphragm.

Feed Requirements. A range of typical feed stream composition requirements for membrane and diaphragm cells are shown in Table 3. Diaphragm cells are generally tolerant of

Table 3. Brine Feed Requirements for Typical Membrane and Diaphragm Cells^a

Parameter	Upper Limit (mg/kg) ^b	
	Membrane	Diaphragm
Al	0.1	0.5
Ba	0.5	5
Ca + Mg	0.02	5
F	0.5–1	1
Fe	0.1–1	0.3–0.5
Hg	0.2–0.5	1
I	0.2	
Mn	0.05	0.01
Ni	0.1–0.2	0.1
Pb	0.05	
SiO ₂	5	0.5–15
Sr	0.4	5
CO ₃	0.4 g/L	
Na ₂ SO ₄	4–8 g/L	5 g/L
NaClO ₃	10–25 g/L	
TOC	1	1
pH	2–11	2.5–3.5

^aCompiled from refs 21, 27, and 24. ^bLimits differing by an order of magnitude or more are bold and italic.

a less pure feed than membrane cells, particularly so evidenced by the numbers in bold and italic, which differ by at least 10 times. Membrane brine requirements are somewhat specific to the particular membrane chemistry; exact requirements are specified by individual manufacturers. Table 7.10 in ref 24 is an excellent summary of impurity sources, effects, and mitigation strategies.

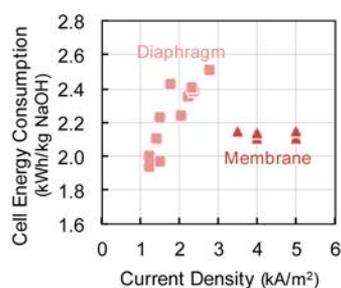
Group II cations, namely, Ba, Ca, Mg, and Sr, are among the most problematic of impurities. All form sparingly soluble hydroxide precipitates, and some can form sparingly soluble sulfates, silicates, iodides, and periodates as well.²⁴ These precipitates restrict flow through the porous diaphragm³² and affect membrane selectivity and electrical resistance.³³ Similar precipitation phenomena set limits on Fe and Ni concentrations, as well as Al, which can drive aluminum silicate and calcium aluminosilicate formation.

Several of the remaining compounds in Table 3 can adversely affect the electrodes or electrolytic processes. Fluoride can corrode titanium-coated anodes.³⁴ Organics cause foaming and can damage electrodes.^{35,36} Magnesium, in addition to its role in causing harmful precipitates, can also cause anodic hydrogen evolution, which reacts explosively with the chlorine gas.

Chlorate and mercury limits are set by indirect effects on the cells. Both can hamper the effectiveness of ion exchange resins that remove hardness, ultimately resulting in the formation of divalent metal precipitates discussed above. Mercury can also deposit on the membrane-cell cathodes,³⁵ although it is only

likely to be present when plants feed both mercury and membrane cells with a single brine stream.

Energy Consumption. Both the diaphragm and membrane processes require steam (or another heat source) and electricity; some typical values are shown in Figure 7. The



	Diaphragm	Membrane
Electricity (kWh _e /kg NaOH)	1.94–2.51	2.10–2.15
Current Density (kA/m ²)	1.21–2.74	3.5–5
Heat, as Exergy (kWh _e /kg NaOH)	0.128–0.196	0.038–0.047
Efficiency	61–80%	75–77%

Figure 7. Energy consumption of chlor-alkali cells depends on the operational current density; values from manufacturers are shown in the inset figure. For the same current density (system size), membrane cells consume less energy. Membrane-based processes also produce purer, more concentrated NaOH, necessitating less steam for evaporation postcell. Data adapted from refs 21 and 27.

diaphragm process uses steam to drive the post-treatment fractional crystallization and concentration processes. The membrane process uses steam for postcell caustic soda concentration. Electricity makes up the greatest portion of overall energy consumption, mostly consumed by the cell itself.

Electrical energy consumption varies by cell design/manufacturer, system size, and operation. At larger system sizes, with equivalently lower current density, energy consumption is lower, but capital expenditures are higher.²¹ Economic optimization therefore sets the operating point. Operational wear and cell age also play a role: energy consumption may increase by about 5% after three years of operation.²¹

Bipolar Membrane Electrodialysis. Bipolar membrane electrodialysis (EDBM) uses a repeating sequence of anion exchange membranes (AEM), cation exchange membranes (CEM), and bipolar membranes (BM) to separate a salt into its component acid and base. Figure 8 shows the process schematically. The bipolar membrane electrolyzes water, and the alternating arrangement of the AEMs and CEMs then trap salt cations and anions in channels with protons and hydroxide ions. The result is alternating channels of acid, base, and diluted salt.

The functionality-enabling keystone in the EDBM process is the bipolar membrane. Bipolar membranes are primarily composed of three different layers, a strong acid cation exchange membrane, a weak base layer, and a strong base anion exchange membrane.³⁷ Further developments and their applications are discussed by Kumar et al.³⁷

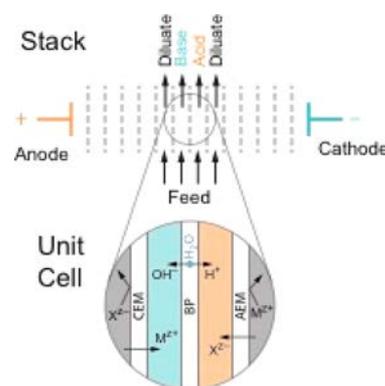


Figure 8. Bipolar membrane electrodialysis uses water-splitting bipolar membranes combined with alternating anion and cation exchange membranes to sort feed salt cations and anions into acid and base streams.

Numerous recent experimental studies have demonstrated recovery of NaOH and HCl with a broad concentration range from 0.2 to 1.5 M and 0.2 to 1.3 M, respectively. Table 4 summarizes these studies, with entries including water production type, feed and experimental operating conditions, product recovery, and energy consumption. Recovery of NaOH and HCl depends upon many factors related to system design and operation as well as the properties of the feedwater. In particular, salinity is important. For example, desalination retentates of RO plants producing drinking water^{40,41} and high NaCl-containing industrial wastewater^{38,39,42,43} show differences in performance. In addition, recovery can be limited by the membrane properties themselves, as is the case of feed streams containing other constituents such as total organic carbon and metals (Table 4).

Recently, Davis et al. showed the production of NaOH (0.3 M) and HCl (0.3 M) from a diluted salt solution.³⁹ Interestingly, a preliminary cost analysis on purchasing vs in situ production predicted a reduction from 21 to 3.5–12.6 USD/kmol for NaOH and from 37 to 3.5–12.6 USD/kmol for HCl.

Finally, comparison of the experimental studies in Table 4 is challenging because of varying reactor configurations or operational strategies and varying methodologies used. Nevertheless, such a comparison would be useful in providing the basis for further experimental designs.

Challenges for EDBM Integration at Scale. Bipolar membrane electrodialysis is scientifically recognized as a suitable technology and shows technical and economic advantages.⁴⁴ However, in practice, its use is limited. The reasons possibly limiting the wide adoption of this technology are mainly membrane and electrode cost, scaling caused by salts, and overall robustness. After a careful literature review, from our viewpoint, the real bottlenecks can be summarized as follows:

1. The cost of bipolar membranes and electrodes as illustrated by Strathmann⁴⁵ and Xu and Huang.⁴⁶ The cost of bipolar membranes is 3–10 times higher than monopolar membranes.^{47,48}
2. The robustness of the technology in terms of dealing with the high salt concentration in brines (i.e., Ca²⁺ and Mg²⁺) is a limiting step.

Table 4. Summary of EDBM Experiments Producing HCl and NaOH from NaCl Streams

Feed and Experimental Conditions ^a				Product Recovery			Energy Consumption ^a		
Water Type	NaCl Conc. (M)	Other Const.	Current Dens. (A/m ²)	Current Eff. (%)	Max NaOH Conc. (M)	Max HCl Conc. (M)	NaOH (kWh _e /kg)	HCl (kWh _e /kg)	ref
Fresh	n.a.		1000	53.9–65.7	1.5	1	3.5–4.5	4.12–4.94	42
Industrial	0.019	24 mg/L TOC, Metals	100–900	40–90	0.2	0.2	n.a.	n.a.	40
Fresh	1	0.06 M SO ₄ ²⁻	250–1000	50–80	0.02	0.8	n.a.	n.a.	40
Fresh	0.65	0.04 M SO ₄ ²⁻	340–570	52–74	1	1.2	n.a.	7.5–9.3	71
Fresh	n.a.	Conductivity 40 mS/cm; Mg ²⁺ and Ca ²⁺ <1 mg/L		35–60	1	0.5–1.3		4.7–8	43
Evaporative Cooling	0.05–4	n.a.	26–260	10–100	0.3	0.3	n.a.	n.a.	39

^an.a.: not available or difficult to interpret; TOC: total organic carbon.

- Product purity and demonstrations for several months to multiyear performance due to strong bases and acids are yet to be proved.⁴⁹
- Transport losses of H⁺ and OH⁻ can influence overall efficiency.^{49,51}
- Fouling caused by organic matter and silica is an issue.
- Small-scale production and limited technical support for bipolar membranes is another issue.

Future Directions. Bipolar membranes electro dialysis has opened the possibility to recover NaOH and HCl in situ. Future research must focus on finding cheaper (selective) bipolar membranes and electrodes. As scaling and fouling is of special importance in the operation, therefore, strategies to minimize these problems should be a focal point. In addition, research should also focus on ion exchange resins and product purity. Finally, for technological developments and financial implications, future research should focus on modeling and process design, taking several aspects into consideration such as costs, ease to control fouling/scaling, and transport losses.

Direct Electrosynthesis. Direct anodic electrochemical HCl production by water electrolysis has been challenging due to electrodes functionality (commercially available electrodes are prone to chlorine formation). Lin et al. developed a novel system using a Mn_{0.84}Mo_{0.16}O_{2.23} oxygen evolution electrode simultaneously generating HCl and NaOH from NaCl during water electrolysis.⁴⁹ Lin et al. report anodic generation of protons at a high Coulombic efficiency (CE) (≥95%) along with the production of chlorine for 3% to 5% of the supplied current.⁴⁹ In addition, HCl was produced (moderate strengths) at a CE of 65 ± 4% with a CE of 89 ± 1% for cathodic caustic production. Production of NaOH and HCl depends upon many factors related to the coating of the electrode and oxygen efficiency, design, and operation. In addition, oxide formation on the electrode⁵⁰ and acid-blocking membranes⁵¹ can further improve the process.

Challenges for Direct Electro-Synthesis at Scale. Direct electro-synthesis is an emerging technology (so far proof-of-concept only) for the production of chemicals. This technology will be at some point used because of simultaneous production of NaOH and HCl. From our viewpoint, the challenges can be summarized as follows:

- The oxygen efficiency of the coating is rather limited and needs further improvements.
- The dilute nature of the products requires a large storage volume.
- Results are only from artificial brines as a proof-of-concept; therefore, experimental demonstration with actual brine is still needed.

- Long-term performance of the electrode coating has not yet been demonstrated.
- Oxide accumulation on the electrode surface is challenging.
- Transport of H⁺ ions (crossover) is an issue and can influence productivity and overall efficiency.^{49,51}
- The effect of chlorine on anion exchange membranes needs further investigation.

Future Directions. Direct electro-synthesis has opened the possibility to produce NaOH and HCl simultaneously. Future research must focus on finding better electrode coating and chlorine-resistant anion exchange membranes. As oxygen efficiency is of special importance in the operation, strategies to improve efficiency should be pursued. In addition, research should also focus on either producing concentrated products or concentration. For real world applications, technological developments, and financial implications, future research should focus on using actual brines. Finally, modeling and process design should be explored.

Review of Available Technologies for Brine Concentration. In this section, we briefly compare some available technologies for Block 2, brine concentration (Figure 3), including the established technologies multiple effect evaporation/distillation (MEE/MED), mechanical vapor compression (MVC), electro dialysis (ED), and reverse osmosis (RO), as well as the emerging technologies membrane distillation (MD)^{52–59} and humidification-dehumidification (HDH).^{60–69} We focus primarily on energy consumption, which is a significant portion of system cost. Some benchmarks for each technology follow.

These technologies are all used for desalination—both brine concentration and desalination split a saline feed into streams of greater and lesser concentration—but key figures of merit differ by application. Here, the concentration factor, CF = $w_{\text{NaCl},c} / w_{\text{NaCl},f}$ is the target figure of merit. The SWRO brine salinity is fixed (approximately 7% NaCl w/w) and the chlor-alkali process requires a saturated brine feed (26% NaCl w/w) to avoid oxygen evolution at the anode. Thus, the brine concentration step must achieve CF = 0.026/0.07 = 3.71. Bipolar membrane electro dialysis can operate with or without brine concentration; the level of brine concentration affects the attainable caustic soda concentrations.

For CF = 26/7, the minimum recovery ratio is 73% by mass conservation of salt. If significant salt passage occurs, the required recovery ratio increases according to

$$RR = \frac{CF - 1}{CF - SP} \quad (11)$$

where CF is the concentration factor and SP is the salt passage, the ratio of product-to-feed salt concentration. Unlike drinking water desalination, SP has no effect on the product (NaOH) quality, so it is unconstrained. The recovery ratio is also less important than in drinking water desalination since (1) there is vast excess brine available and (2) the existing brine outfall has sufficient capacity for any flow we choose to redirect to the NaOH plant; the cost of salty product disposal is restricted to pumping. Both of these variables can thus be optimized to minimize energy and cost.

Energetic benchmarks for brine concentration also differ from desalination. For this application, it makes more sense to report energy consumption as kWh_e/t concentrate since the concentrate, not the fresh water, is the valuable product. Division by RR/(1 - RR) converts kWh_e/t concentrate to kWh_e/t fresh water.

To provide a fairer baseline for comparison between heat- and work-driven systems, we convert thermal energy consumption values to exergetic equivalents. To do so, we multiply the specific heat input by the Carnot efficiency for a heat engine operating between the dead state temperature, T₀, and the system top brine temperature, TBT. For systems with performance reported as a Gained Output Ratio (GOR), the conversion is

$$\text{kWh}_e/\text{t concentrate} = \frac{\text{RR}}{\text{GOR}(1 - \text{RR})} \left(1 - \frac{T_0}{\text{TBT}} \right) \quad (12)$$

The GOR is defined as

$$\text{GOR} = \frac{\dot{m}h_{fg}}{\dot{Q}_i} \quad (13)$$

where $\frac{\dot{Q}_i}{\dot{m}_w}$ is the heat input to the system per unit fresh water produced, and h_{fg} is the enthalpy of vaporization of water.

For a typical SWRO brine stream, approximated as a 7% w/w NaCl solution, concentration to 26% w/w with perfect salt rejection requires ca. 3.7 kWh_e/t of fresh water, or about 10 kWh_e/t concentrate (Figure 9). For less than 100% salt rejection, the minimum energy required is smaller. Consequently, systems that “partially” desalinate may also run for lower energetic cost.

Using models in literature³¹ for RO, MVC, MEE, HDH, and PGMD, we can compare ranges of energy consumption for

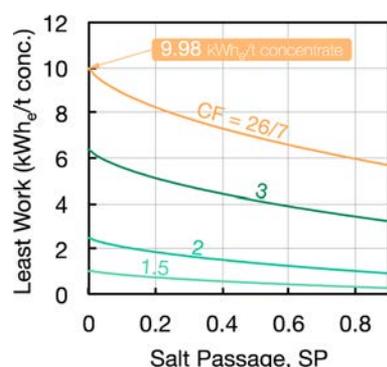
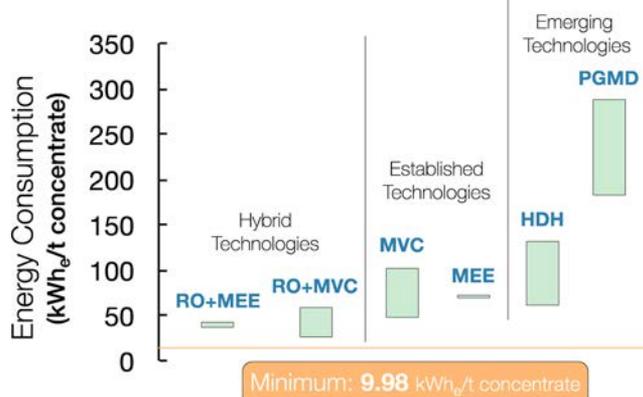


Figure 9. In brine concentration, unlike desalination, the less-saline product stream may acceptably contain salt. This nonzero salt passage may reduce energy requirements but will require greater recovery ratios to achieve the target concentration factor.

typical operating conditions. A summary plot of model-predicted energy consumption values is shown in Figure 10.



*RO Salinity: 7% → 11.5% (120 bar)

RO + (Thermal)		MVC	
TPD	0.5–10 bar	TBT	60 °C
η_p	0.85	η_{co}	0.6–0.8
η_{ERD}	0–0.9	TTD	1–5 K
Most sensitive variables: ERD		Most sensitive variables: η_{co} , TTD	

MEE		HDH (0-Ext)		PGMD	
N	3	PPTD	1–5 K	PPTD	1–5 K
TBT	70 °C	TBT	70 °C	TBT	70 °C
TTD	1–5 K	Ext.	0	Most sensitive variables: PPTD	
Most sensitive variables: N		Most sensitive variables: PPTD			

Figure 10. Typical ranges of brine concentration energy consumption, reported on an exergetic basis for the range of system parameters shown in the tables.

Energy consumption is reported as equivalent electricity consumption (kWh_e) normalized by the mass flow rate of concentrate, which is the useful system output. Heat inputs to systems are converted to equivalent electricity on an exergetic basis. To do so, we multiply the specific heat input by the Carnot efficiency for a heat engine operating between the brine concentration system’s bottom and the top temperatures, as discussed at the beginning of the section.

As seen in Figure 10, hybridization with high-pressure RO can provide a significant energetic benefit to thermal brine concentrators. Although the developing technologies generally consume more energy, that does not necessarily imply economic advantage, particularly in cases where much cheaper materials; for example, plastic can drive down capital expenditures. We also see that many of the developing technologies have wider energy consumption ranges, indicating uncertainty in optimal operating parameters.

Review of Previous Pilot and Full-Scale Studies. In this section, we review four plants that electrolyze seawater or seawater concentrate to produce caustic. One plant operates at commercial scale⁷⁰ and uses the chlor-alkali process. [In a feasibility study, Al-Mutaz and Wagialla⁷⁷ reference an additional full-scale plant, but we were unable to find further details in the open literature. The plant, located in Abu- Dhabi,

uses NaCl crystallized from desalination plant brine to feed chlor-alkali cells. The $\text{H}_2(\text{g})$ and $\text{Cl}_2(\text{g})$ are reacted to make hydrochloric acid.] The other three are lab or pilot scale^{71–73} and employ bipolar membrane electro dialysis. Numerous other relevant case studies^{74,75} and experimental works^{40,41,76} do exist in the literature. However, we focus here on those that use *real*—not synthetic—SWRO brine, as the authors believe that compositional differences between real SWRO brine and pure NaCl solutions drive the technoeconomic challenge for scaleup.

Kobuchi 1983. The first plant to use seawater to feed the chlor-alkali process was built in Kuwait in the 1980s.⁷⁰ The facility employs standard membrane-based electrolysis to manufacture caustic, as well as chlorine gas, liquid chlorine, hydrogen gas, hydrochloric acid, and sodium hypochlorite. The HCl is produced by direct synthesis, and some is used internally. Nearby facilities use some of the chlorine and sodium hypochlorite for water disinfection.

The feed to the chlor-alkali process is based on ED and MEE technology used for edible salt production in Japan. Seawater is fed through gravity sand filter and secondary filtration pretreatment processes and then concentrated—but not desalinated—using ED. Crystallization of NaCl then occurs in a triple-effect, backward-feed evaporator. A portion of this product NaCl is dried and stored; the remaining wet salt is blended with dry salt and pure water to feed a saturated brine to the chlor-alkali cells.

The brine concentration step (ED) produces concentrated seawater with 205 g/L NaCl for an energetic cost of 205 kWh_e/t NaCl. The specifications of the chlor-alkali process are not given, but the plant is reported to use standard membrane chlor-alkali technology.

Yang 2014. Yang et al. uses bipolar membrane electro dialysis (EDBM) on softened RO concentrate to produce mixed acid and base streams.⁷¹ The RO brine was taken from the desalination facility at the Huangdao power plant in Qingdao, China. Brine pretreatment to the EDBM was softening by NaOH to remove hardness and acidification using HCl to prevent AEM fouling. The brine was not concentrated. The EDBM unit contains three cell pairs with AEMs and CEMs from Qinaqiu Environmental Protection & Water Treatment Corp. and the bipolar membranes from FuMA-Tech GmbH.

The setup produced mixed acids at about 0.67 mol/L and a mixed base of about 0.4 mol/L at a purity around 12 g of NaCl/kg NaOH, which meets EU standards.¹⁷ Most of the mixed acid was HCl; most of the mixed base was NaOH. Energy consumption was about 9 kWh_e/kg acid, or about 14 kWh_e/kg NaOH, which equates to an efficiency of about 3%.

Reig 2016. Researchers at the Polytechnic University of Catalonia have published several works on using bipolar membrane electro dialysis to produce salts, acids, and bases from various wastewaters, including SWRO brine. Two recent studies^{72,73} demonstrated HCl and NaOH production from real SWRO brine using two different brine purification/concentration steps: nanofiltration and electro dialysis. Both studies used identical three-cell bipolar ED (EDBM) units (sourced from PCCell GmbH), and both used brine from the El-Prat desalination plant in Barcelona, Spain.

The first study⁷² uses NF and softening to purify the SWRO brine. Filtered brine is sent to NF, yielding a permeate with reduced multivalents and at slightly lower NaCl concentration (59 g/L to 52 g/L), which is in turn softened and sent to the EDBM unit. The NF uses five four-inch NF270 elements in

series operated between 8 and 20 bar for at least 5 days. Softening is by Na_2CO_3 and NaOH. Notably, there is no brine concentration. The authors report energy consumption between 2.3–2.9 kWh_e/kg NaOH, which according to our model equates to 18–21% efficiency. Caustic concentrations range from about 2.6%–4.1% w/w, which may not meet all plant requirements (Table 1). No quantitative data are reported on impurities. However, the EDBM unit employs monovalent-selective cation and anion exchange membranes, meaning multivalent ion concentrations are lower in the acid and base streams than in the salt feed.

Monovalent-selective electro dialysis is used in the second work⁷³ to simultaneously purify and concentrate SWRO brine. The ED concentrate loop is recirculated to attain 100 and 200 g of NaCl/L streams fed to the EDBM step. Reported energy consumption ranged from 2.3–3.6 kWh_e/kg NaOH, for which we estimate efficiencies between 14% and 22%. NaOH concentrations between 26.4–85.6 g NaOH/L (about 3–7.5% w/w) were achieved.

From the limited brine purification compared to chlor-alkali, it may appear that EDBM has higher tolerance for hardness. However, the stringent hardness limits in chlor-alkali are set by, for example, $\text{Mg}(\text{OH})_2$ solubility in NaOH solutions, which drastically decreases with increasing NaOH concentration. Consequently, when producing lower concentrations of NaOH, higher hardness is tolerable.

■ CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDY

Conclusions. Producing NaOH from SWRO brine for reuse within the desalination plant has the potential to benefit the environment and plant owner/operator bottom line. By reviewing representative plant requirements, performing a benchmark thermodynamic process analysis, surveying available technologies, and examining existing lab and commercial-scale facilities, we have reached the following conclusions. The subtitles below correspond with the section in the article body in which the conclusion was discussed. Ultimately, with improved product purity and increased product concentration, bipolar membrane electro dialysis and direct electro synthesis have the potential to energetically outperform chlor-alkali.

On Process Requirements.

- Typical large-scale SWRO plants consume tens to hundreds of dry tons of NaOH per year at concentrations between 3% and 26%.
- The NaOH produced must meet site-relevant drinking water standards and regulations. Standard EN896 prescribes purity requirements for EU facilities. Based on typical seawater composition, the standard's limits on minor impurities (e.g., trace metals) are not likely to be exceeded.

On Process Limits and Thermodynamics.

- For SWRO brine abstracted as 7% w/w NaCl, the process will produce a maximum of ca. 48 g of NaOH/kg brine and ca. 44 g of HCl/kg brine or 42 g of $\text{Cl}_2(\text{g})$ and 1.2 g of $\text{H}_2(\text{g})$.
- Production of NaOH from NaCl is energy intensive and depends strongly on the required NaOH concentration and the byproducts. For processes with byproducts $\text{Cl}_2(\text{g})$, $\text{H}_2(\text{g})$, and between 30–50% NaOH, thermodynamics dictates a minimum of 1.56–1.64 kWh_e/kg NaOH. A process that instead has 10–30% w/w HCl

byproduct has lower minimum energy: between 0.65 and 0.81 kWh_e/kg NaOH. These figures are particularly important because energy is a large, sometimes dominant, portion of the NaOH production cost.

- Brine concentration and/or caustic soda concentration may be required to achieve the desired NaOH concentration, but both consume a relatively small portion of the thermodynamic minimum energy: up to 0.06 kWh_e/kg NaOH (brine conc.) and 0.14 kWh_e/kg NaOH (caustic conc.), depending on desired feed and concentrate concentrations.

On NaOH Production Technologies.

- The chlor-alkali process is a mature technology that will fulfill all purity and concentration requirements. Modern membrane cells require extensive brine purification, most stringently to reduce hardness to ppb levels. Membrane-based processes produce 50% w/w NaOH and consume 2.1–2.2 kWh_e/kg NaOH on an exergetic basis, which equates to 75–77% efficiency, according to our model.
- Bipolar membrane electrodesialysis is an emerging technology that uses bipolar membranes to split salt into its acid and base. It has the potential to consume less energy than chlor-alkali, but based on the literature surveyed, the lowest energy consumption is 2.3 kWh_e/kg NaOH for weakly concentrated NaOH—still greater energy consumption and lower concentration NaOH than state of the art chlor-alkali.
- Based on currently demonstrated technology, it appears the major trade-offs between chlor-alkali and bipolar membrane electrodesialysis are as follows. Chlor-alkali requires less energy but more extensive brine purification and concentration. EDBM requires more energy but has a lower thermodynamic minimum. EDBM requires less brine purification and concentration but largely because it produces less concentrated caustic soda. (Many seawater solutes have lower solubility at higher NaOH concentrations.)

On Brine Concentration Technologies.

- So-called partial desalination can provide an energetic advantage since the minimum energy for brine concentration depends on salt passage. Unlike desalination, brine concentration does not specify diluant stream quality. For concentration of SWRO brine to saturation, the minimum energy can be reduced from 10 to 6 kWh_e/t concentrate by allowing up to 80% salt passage. The cost is a higher required recovery ratio.
- Many desalination technologies can be used in brine concentration applications, but some are not well-developed at small scale. New high-pressure RO elements can be hybridized with thermal technologies to reduce energy consumption.

On Existing Lab, Pilot, and Full-Scale Systems.

- Large-scale production of NaOH from seawater concentrates is technically proven using ED and the membrane chlor-alkali process. The NaOH from this process meets or exceeds typical and concentration requirements.
- Lab-scale production of NaOH from seawater concentrates by bipolar membrane electrodesialysis is technically proven. The concentration of NaOH produced by these processes is only sufficient for some users. The data on

purity is limited such that we cannot evaluate whether the NaOH meets purity requirements.

Recommendations. Based on the requirements for internal reuse and the conclusions above, we believe there is potential for EDBM as a scalable solution for NaOH production using SWRO brine. We believe the following are among the most needed research for realization.

- EDBM design improvements are needed to increase energy efficiency and achieve values closer to the standard-bearer: chlor-alkali. Only then will EDBM be able to capitalize on its lower minimum energy to drive down NaOH production cost.
- Studies to elucidate the pretreatment requirements for EDBM systems and the relationship between EDBM feed and product quality are needed. Such work is required to inform pretreatment design and determine overall process technoeconomic feasibility. More experimental studies on nanofiltration and other brine purification techniques using real seawater concentrates are needed to understand performance at high salinity and diverse composition.
- Modeling and experimental work on scalable partial desalination technologies, such as novel ED processes, at high salinity with real seawater concentrates are needed. Novel cell arrangements that use, for example, monovalent selective membranes to combine brine purification and concentration may prove advantageous.
- Development of higher pressure RO should continue.
- Long-term operational studies of any pilot system are needed to verify system robustness and product quality over industrially relevant time scales.

APPENDICES

A. Least Work Analysis

For an open system in steady state, the First Law of Thermodynamics is

$$\dot{Q} + \dot{W} + \sum_i \dot{H}_i - \sum_o \dot{H}_o = 0 \quad (\text{A1})$$

where \dot{Q} and \dot{W} are the net heat and work transfer rates across the control volume (CV) boundary,¹ respectively; and \dot{H}_i and \dot{H}_o are the net enthalpy inflows and outflows, respectively. The Second Law of Thermodynamics is

$$\frac{\dot{Q}}{T_b} + \sum_i \dot{S}_i - \sum_o \dot{S}_o + \dot{S}_{gen} = 0 \quad (\text{A2})$$

where \dot{S}_i and \dot{S}_o are the net entropy inflows and outflows, respectively; T_b is the temperature of the control volume boundary; and \dot{S}_{gen} is the entropy generation rate within the control volume.

We choose the control volume boundary such that it and streams crossing it are in thermal equilibrium with the environment, i.e., $T_b = T_0$ and \dot{H}_i , \dot{H}_o , \dot{S}_i , and \dot{S}_o are all evaluated at T_0 . Then, multiplying eq A2 by T_0 and subtracting it from eq A1, the cross-boundary heat transfer terms cancel, and

$$\dot{W} = \sum_o [(\dot{H} - T_0\dot{S})]_o - \sum_i [(\dot{H} - T_0\dot{S})]_i + T_0\dot{S}_{gen} \quad (\text{A3})$$

The work required reaches a minimum in the reversible limit, or where entropy production is zero. In addition, since we have chosen enthalpy H and entropy S to be evaluated at T_0 , the term in the parentheses collapses to the specific Gibbs free energy, $G = H - TS$. We are thus left with the following simple expression for the minimum work input, or reversible work:

$$\dot{W}_{\text{rev}} = \sum_o \dot{G}_o - \sum_i \dot{G}_i \quad (\text{A4})$$

where \dot{G} is the flow rate of Gibbs free energy across the CV boundary. Equation A4 is the form we use in the least work analyses of process variants A and B.

On the temperature–pressure domain bounded by 5 and 95 °C and 0.1–10 bar, evaluated using the Redlich–Kwong equation of state,⁷⁸ the fugacity coefficient of $\text{Cl}_2(\text{g})$ ranges from 0.901 to 0.999. For $\text{H}_2(\text{g})$, it ranges from 1.000 to 1.006. In the light of these results, we take the fugacity coefficient as unity throughout this work. We use Hamer and Wu's model⁷⁹ to evaluate NaOH, NaCl, and HCl activity and osmotic coefficients.

A.1. Variant A. Applying eq 6 to a control volume defined by the combined green and blue areas in Figure 3 yields

$$\dot{W}_{\text{rev}} = \dot{G}_2 + \dot{G}_4 + \dot{G}_5 + \dot{G}_6 - \dot{G}_1 \quad (\text{A5})$$

We next break each \dot{G} into its components, apply mass conservation, noting that by stoichiometry, $\dot{n}_{\text{NaCl},1} = 2\dot{n}_4 = 2\dot{n}_5 = \dot{n}_{\text{NaOH},6}$ to find

$$\begin{aligned} \dot{W}_{\text{rev}} = \dot{n}_{\text{NaOH},6} & \left(\frac{1}{2} \mu_{\text{H}_2,4} + \frac{1}{2} \mu_{\text{Cl}_2,5} + \mu_{\text{NaOH},6} - \mu_{w,1} \right. \\ & \left. - \mu_{\text{NaCl},1} \right) + \dot{n}_2 (\mu_{w,2} - \mu_{w,1}) + \dot{n}_{w,6} (\mu_{w,6} - \mu_{w,1}) \end{aligned} \quad (\text{A6})$$

Expanding the chemical potential terms, normalizing by $\dot{n}_{\text{NaOH},6}$ and simplifying yields

$$\begin{aligned} \frac{\dot{W}_{\text{rev}}}{\dot{n}_{\text{NaOH},6}} = RT & \left[\frac{\Delta_r G_A^\circ}{RT} + \ln \left(\frac{p_{\text{H}_2}^{1/2} p_{\text{Cl}_2}^{1/2} a_{\text{NaOH},6}}{p^\circ a_{w,1} a_{\text{NaCl},1}} \right) \right. \\ & + \left(\frac{1 - x_{\text{NaCl},1}}{x_{\text{NaCl},1}} - \frac{1}{x_{\text{NaOH},6}} \right) \ln \left(\frac{a_{w,2}}{a_{w,1}} \right) \\ & \left. + \left(\frac{1 - x_{\text{NaOH},6}}{x_{\text{NaOH},6}} \right) \ln \left(\frac{a_{w,6}}{a_{w,1}} \right) \right] \end{aligned} \quad (\text{A7})$$

where

$$\Delta_r G_A^\circ = \frac{1}{2} \mu_{\text{H}_2}^\circ + \frac{1}{2} \mu_{\text{Cl}_2}^\circ + \mu_{\text{NaOH}}^\circ - \mu_w^\circ - \mu_{\text{NaCl}}^\circ \quad (\text{A8})$$

and $p^\circ = 101,325$ Pa is a reference pressure.

The first two terms in eq A7 represent the chemical reactions occurring within the cell, i.e., the energy required to oxidize Cl^- and the energy to electrolyze water. These terms dominate. The third and fourth terms are associated with changing the state of the water in the feed. The third term represents brine concentration (removal of pure water from the feed), and the fourth term roughly reflects caustic concentration. These terms become more relevant as the brine salt concentration and the final caustic concentration increase.

A.2. Variant B. Applying eq 6 to the combined area shaded green and red yields

$$\dot{W}_{\text{rev}} = \dot{G}_2 + \dot{G}_3 + \dot{G}_7 + \dot{G}_8 - \dot{G}_1 \quad (\text{A9})$$

By breaking each state into its chemical constituents, i.e., $\dot{G}_1 = (\dot{n}\mu)_{\text{NaCl},1} + (\dot{n}\mu)_{w,1}$ and simplifying according to stoichiometry and mass conservation, i.e., $\dot{n}_{\text{Na},p} = \dot{n}_{\text{Cl},q} = \dot{n}_{\text{H},7} = \dot{n}_{\text{OH},8} = \dot{n}_{\text{NaCl},1} = \dot{n}_{\text{NaOH},8}$ for any state p and q , eq A9 becomes

$$\begin{aligned} \dot{W}_{\text{rev}} = \dot{n}_{\text{NaOH},8} & (\mu_{\text{HCl}} + \mu_{\text{NaOH}} - \mu_{\text{NaCl}} - \mu_w) \\ & + \dot{n}_{w,8} (\mu_{w,8} - \mu_{w,1}) + \dot{n}_{w,7} (\mu_{w,7} - \mu_{w,1}) \\ & + \dot{n}_{w,2} (\mu_{w,2} - \mu_{w,1}) \end{aligned} \quad (\text{A10})$$

As with the analysis for Variant A, we normalize by the product caustic flow rate to find the final expression for least work as a function of desired NaOH and HCl concentrations:

$$\begin{aligned} \frac{\dot{W}_{\text{rev}}}{\dot{n}_{\text{NaOH},8}} = RT & \left[\frac{\Delta_r G_B^\circ}{RT} + \ln \left(\frac{a_{\text{NaOH},8} a_{\text{HCl},7}}{a_{\text{NaCl},1} a_{w,1}} \right) \right. \\ & + \left(\frac{1 - x_{\text{NaOH},8}}{x_{\text{NaOH},8}} \right) \ln \left(\frac{a_{w,8}}{a_{w,1}} \right) + \left(\frac{1 - x_{\text{HCl},7}}{x_{\text{HCl},7}} \right) \ln \left(\frac{a_{w,7}}{a_{w,1}} \right) \\ & \left. + \left(\frac{1}{x_{\text{NaCl},1}} - \frac{1}{x_{\text{NaOH},8}} - \frac{1}{x_{\text{HCl},7}} \right) \ln \left(\frac{a_{w,2}}{a_{w,1}} \right) \right] \end{aligned} \quad (\text{A11})$$

where

$$\Delta_r G_B^\circ = \mu_{\text{HCl}}^\circ + \mu_{\text{NaOH}}^\circ - \mu_{\text{NaCl}}^\circ - \mu_w^\circ \quad (\text{A12})$$

Like Variant A, the first two terms in eq A11 reflect the energy required to break bonds, separating NaCl and H_2O into NaOH and HCl. Again, like Variant A, this term dominates. The remaining three terms deal with acid, base, and brine concentration, respectively.

A.3. Caustic Concentration. Applying eq 6 to the control volume in the Figure 5 inset, we find

$$\dot{W}_{\text{rev}} = \dot{G}_w + \dot{G}_c - \dot{G}_f \quad (\text{A13})$$

As with the previous analyses, we break out the \dot{G} terms like $\sum_j \dot{n}_j \mu_j$ and simplify, conserving mass and caustic:

$$\dot{n}_f = \dot{n}_c + \dot{n}_w \quad (\text{A14})$$

$$\dot{n}_f x_{\text{NaOH},f} = \dot{n}_c x_{\text{NaOH},c} = x_{\text{NaOH},c} (\dot{n}_f - \dot{n}_w) \quad (\text{A15})$$

With some manipulation, the reversible work for caustic concentration, per mole caustic in the concentrate, is

$$\begin{aligned} \frac{\dot{W}_{\text{rev}}}{\dot{n}_{\text{NaOH},c} RT} & = \ln \left(\frac{a_{\text{NaOH},c}}{a_{\text{NaOH},f}} \right) + \left(\frac{1}{x_{\text{NaOH},f}} - \frac{1}{x_{\text{NaOH},c}} \right) \ln \left(\frac{1}{a_{w,f}} \right) \\ & + \left(\frac{1 - x_{\text{NaOH},c}}{x_{\text{NaOH},c}} \right) \ln \left(\frac{a_{w,c}}{a_{w,f}} \right) \end{aligned} \quad (\text{A16})$$

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Notes

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NOMENCLATURE

Roman Symbols

- a = Activity
 b = Molality, mol/kg
 CF = Concentration factor
 ERD = Energy recovery device
 f = Fugacity, Pa
 \dot{G} = Gibbs energy flow rate, kW
 \dot{H} = Enthalpy flow rate, kW
 h_{fg} = Enthalpy of vaporization, kJ/kg
 \dot{M} = Molar mass, kg/mol
 \dot{m} = Mass flow rate, kg/s
 N = Number of effects
 \dot{n} = Molar flow rate, mol/s
 p = Pressure, Pa
 PPTD = Pinch-point temperature difference, K
 \dot{Q} = Heat transfer rate, kW
 R = Universal (molar) gas constant, kJ/mol·K
 RR = Recovery ratio
 \dot{S} = Entropy flow rate, kW/K
 \dot{S}_{gen} = Entropy generation rate, kW/K
 SP = Salt passage
 T = Temperature, K or °C
 TBT = Top brine temperature, °C
 TPD = Terminal pressure difference, bar
 TTD = Terminal temperature difference, K
 \dot{W} = Work transfer rate, kW
 w = Mass fraction
 x = Mole fraction

Greek Symbols

- η = Efficiency
 γ = Molal activity coefficient
 μ = Chemical potential, kJ/mol
 φ = Molal osmotic coefficient

Subscripts

- 0 = Dead state
 b = Boundary
 c = Concentrate
 co = Compressor
 cw = Cooling water
 ex = Extraction
 f = Feed
 i = Inlet
 ma = Moist air
 o = Outlet
 p = Pump
 rev = Reversible
 s = Steam
 w = Water

Superscripts

- ^o = Reference state

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