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## **Integrated valorization of desalination brine via NaOH recovery: opportunities and challenges**

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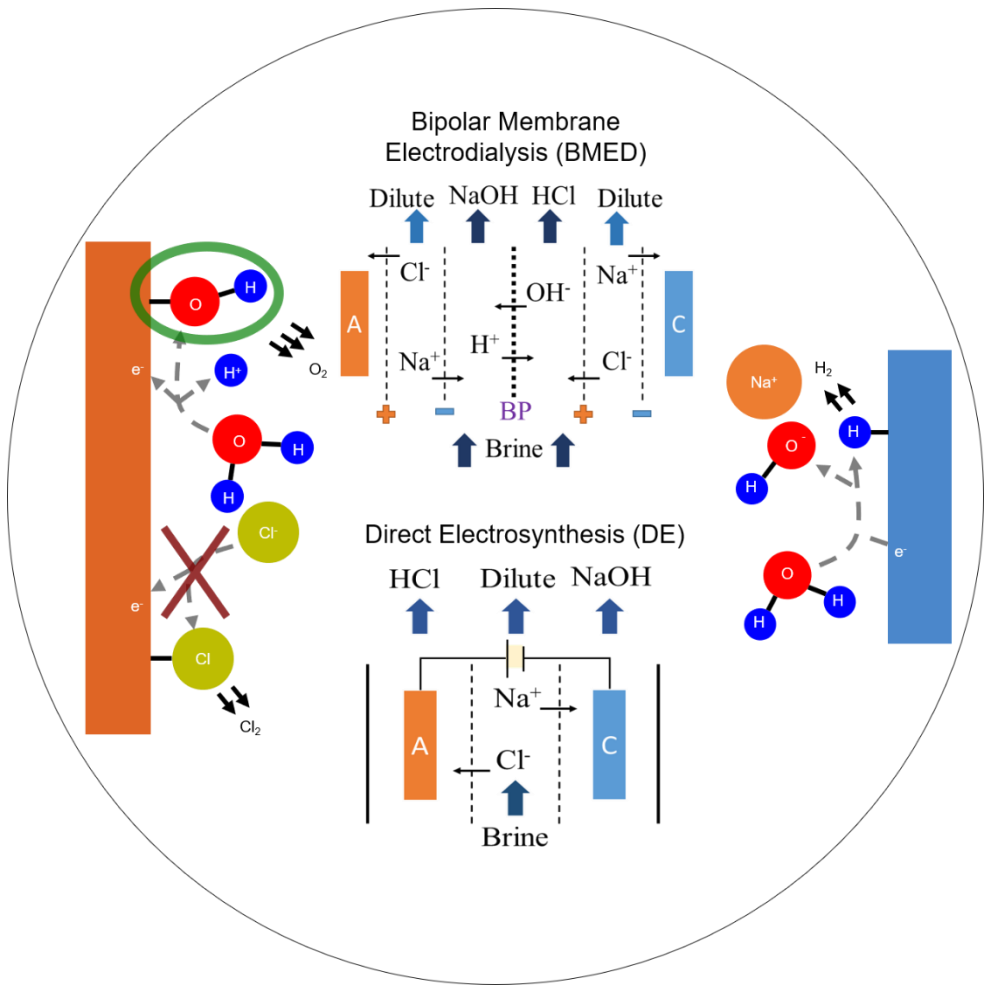
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**Abstract:** The rising use of seawater desalination for fresh water production is driving a parallel rise in the discharge of high salinity brine into the ocean. Better utilization of this brine would have a positive impact on the energy use, cost, and environmental footprint of desalination. Further, intermittent renewable energy can easily power the brine utilization and, for reverse osmosis technology, the entire desalination plant. One pathway toward these goals is to convert the otherwise discharged brine into useful chemicals: waste could be transformed into sodium hydroxide or caustic soda (NaOH) and hydrochloric acid (HCl). In this mini review, we discuss opportunities and challenges for integrated valorization of desalination brine through NaOH and HCl recovery.



TOC Figure.

## 1. Seawater desalination brine as a source of NaOH

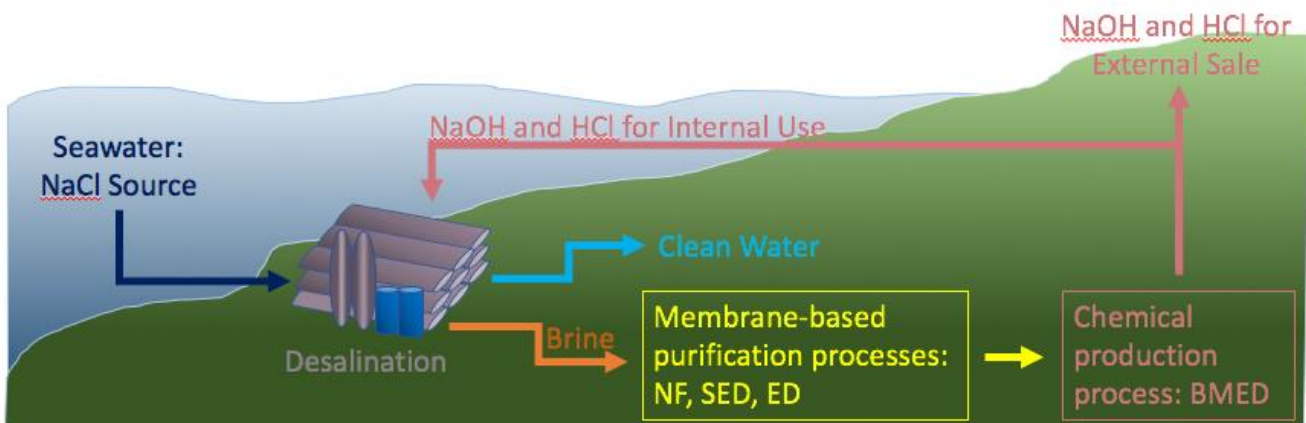
NaOH and HCl are both frequently used in water treatment processes. NaOH, or caustic soda, also has several essential applications in the desalination industry. In seawater reverse osmosis, incoming seawater is treated with caustic soda in order to increase the pH. By increasing the pH of seawater, certain acidic species are rendered less permeable to the reverse osmosis membrane. For example, at around a pH of 9, the borate anion  $B(OH)_4^-$  becomes the dominant aqueous boron species, rather than boric acid, which is harder to reject.<sup>[1]</sup> The same is true for the rejection of silica<sup>[2]</sup> and dissolved inorganic carbon<sup>[3]</sup> when the pH is increased. Furthermore, NaOH is a common ingredient in membrane cleaning solutions for foulants:<sup>[4]</sup> organic fouling of membranes has been shown to decrease at higher pH.<sup>[5]</sup>

Approximately 99.5% of all caustic soda is produced through the chlor-alkali process.<sup>[6]</sup> Three types of chlor-alkali processes currently exist: membrane, diaphragm, and mercury processes.<sup>[7]</sup> Typically, direct current is passed through an aqueous sodium chloride (NaCl) solution, causing an electrochemical reaction that produces NaOH, hydrogen ( $H_2$ ) and chlorine ( $Cl_2$ ). NaCl mining is often accompanied by environmental issues, such as the salination of nearby rivers and aquifers by liquid wastes.<sup>[8]</sup> Alternatively, NaCl brine is produced as a waste stream at desalination plants. As for the chlor-alkali products, the NaOH is used by desalination plants while  $H_2$  is a chemical commodity that is used for hydrogenation reactions and has a marketable potential as a fuel. Furthermore, using an alternative oxidation reaction to  $Cl_2$  production, HCl could be recovered for on-site use.

Thus, desalination plants can save money and reduce their environmental damage by recovering NaOH and HCl from brine, which contains sodium chloride.<sup>[7,9]</sup>

## 2. Membrane-based pretreatment processes for brine valorization

By integrating membrane-based processes, resources in seawater reverse osmosis (SWRO) brine, specifically NaCl, can be recovered as valuable chemical commodities (i.e., NaOH and HCl).<sup>[10,11]</sup> To produce NaOH and HCl, the SWRO brine can first be pretreated through nanofiltration (NF), selective electro dialysis (SED), or electro dialysis (ED), and, subsequently, it can be processed via electro dialysis with bipolar membranes (BMED) into the products of interest (Figure 1).<sup>[12-14]</sup> Each of the pretreatment methods provides a distinct way of valorizing the SWRO brine (Table 1). NF can purify the concentrated brine such that the brine mainly contains monovalent ions. SED separates the monovalent and multivalent ions into two streams. ED creates highly concentrated streams of ionic salts from the brine. The use of NF, SED, or ED as a pretreatment step can enhance the performance of a BMED system, which can lead to the production of profitable chemicals and lower volumes of brine disposal. In this section, we describe these processes to compare the benefits and challenges associated with each.



**Figure 1.** Integrated membrane processes for the valorization of desalination brine. The waste stream, or the SWRO brine, from the desalination plant can be fed into a NF, SED, or ED process for pretreatment. Subsequently, the stream can be treated via BMED for acid and base production.

**Table 1.** Pretreatment Methods

Pretreatment Method	Purpose	Mode of Operation	Resulting Streams	Valorization Method
Nanofiltration	Purification	Pressure-driven	Permeate (mainly monovalent ions) and retentate (mainly divalent ions with some monovalent ions)	Lower concentrations of HCl and NaOH
Selective electrodialysis	Ion Separation	Electrically driven with monovalent-selective membranes	Dilute, monovalent-rich and divalent-rich streams	Different acids and bases
Electrodialysis	Concentration	Electrically driven	Dilute and concentrated streams	Higher concentrations of HCl and NaOH

## 2.1. Nanofiltration (NF)

NF is a pretreatment method that can purify SWRO brine by separating monovalent and divalent ions. In an NF system, the separation is driven by an applied pressure, which results in the transport of monovalent ions across the semipermeable membrane and the rejection of most divalent ions.<sup>[15]</sup> Consequently, the permeate stream contains mainly NaCl while the retentate contains the trace ions and the remaining NaCl. Since only a portion of the NaCl is transferred from the SWRO brine to the NF permeate, integrating NF and BMED results in the production of NaOH and HCl at relatively low concentrations.<sup>[12]</sup> For instance, one study pretreated SWRO brine with NF, and the NaCl concentration decreased from 60 g/L to 50 g/L after pretreatment.<sup>[12]</sup> The maximum resulting concentrations of NaOH and HCl subsequent to BMED were approximately 1 M for each.<sup>[12]</sup>

However, since NF membranes are not perfectly selective, some divalent ions can also pass through the membrane into the permeate. In one study, NF with an applied pressure of 20 bar was only able to reject 50% of the calcium ions ( $\text{Ca}^{2+}$ ) and 71% of the magnesium ions ( $\text{Mg}^{2+}$ ).<sup>[12]</sup> If the concentration of divalent ions, specifically  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , become too large, BMED systems can face the issue of scaling. Scaling, the attachment of inorganic precipitates onto the membrane, causes deterioration of membrane performance and increased energy consumption. In order to prevent scaling and provide a feed with the required purity level for BMED, a subsequent precipitation step may be applied after NF pretreatment. A common method of removing  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  through precipitation is the use of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and NaOH to produce calcium carbonate ( $\text{CaCO}_3$ ) and magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ) salts, which can remove up to 96 and 99% of calcium and magnesium ions, respectively, from the NF permeate.<sup>[12]</sup> The resulting

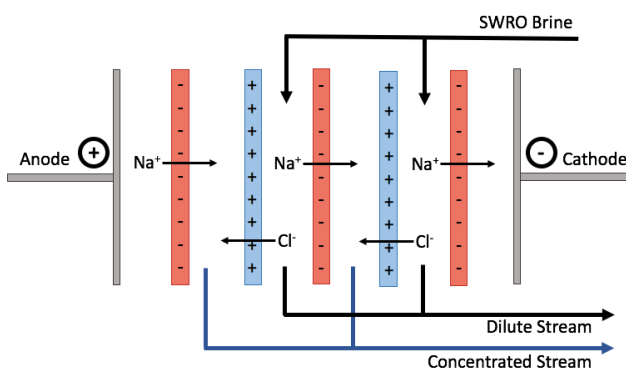
NF permeate stream is then fed into the BMED system to produce NaOH and HCl with negligible scaling.

Alternatively, in search of effective methods to eliminate divalent ions, recent work on cross-linked layer-by-layer polyelectrolyte nanofiltration hollow fiber membranes by Liu et al.<sup>[16]</sup> and Labban et al.<sup>[17]</sup> have demonstrated the selective rejection of multivalent ions at exceedingly low pressures, showing that advanced NF membranes may be useful for removing scalants from the feed stream without the precipitation step. Additionally, carbon nanotube composite and graphene oxide-incorporated polymeric membranes have been proven to exhibit greater mechanical stability and ability to purify water.<sup>[18-20]</sup> In conjunction with different composite materials, others have improved the performance of nanofiltration by exploring different strategies to modify the surface of nanofiltration membranes,<sup>[18-21]</sup> which range from rapid co-deposition of polymers<sup>[21]</sup> to in situ surface reactions<sup>[18]</sup> to inkjet printing.<sup>[19]</sup>

Multiple factors can influence the efficiency of NF systems, including the operating conditions and membrane configuration. Like most membrane-based processes, NF can be operated at different pressures, temperatures, flowrates, and concentrations, which can all affect the energy efficiency and consumption of the process.<sup>[22-24]</sup> Additionally, NF has different configurations, such as flat sheet, spiral-wound,<sup>[25,26]</sup> or hollow fiber.<sup>[27]</sup> While all three configurations have been implemented at the lab-scale, the spiral-wound configuration is the most prevalent in industrial settings. Reig et al. studied the reliability of a lab-scale flat sheet configuration to approximate the results of an industrial-scale spiral-wound configuration.<sup>[25]</sup> While the flat sheet membrane had a high transmembrane flux, the ion rejections and membrane permeances were similar between the two configurations. Generally, the mass transfer and process efficiencies of membrane-based processes can be mathematically modelled to provide approximations of the optimal operating conditions and configurations. Several studies have developed models for NF by considering its properties such as recirculation, ion rejection, permeate production, and energy consumption;<sup>[9,27,28]</sup> as a result, trends between the different factors were identified. By identifying the optimal operating mode and conditions, NF may be a favored pretreatment method for SWRO brine in large-scale use.

## 2.2. Electrodialysis (ED)

Pretreatment through ED concentrates the ions into one stream, which simultaneously dilutes the brine stream (Figure 2). In ED, the anodes and cathodes use electrical force to drive the movement of cations and anions, respectively, through charge-selective cation exchange membranes (CEMs) and anion exchange membranes (AEMs). The ED system has two compartments: one contains the feed stream and the other contains the concentrated stream. Due to the migration flux driven by the potential between the two electrodes, the ions move out of the feed stream and into the concentrated stream. As a result, the feed stream becomes more diluted while the concentrated stream accumulates more ions.



**Figure 2.** Schematic drawing of an ED System. ED has an alternating sequence of CEMs and AEMs, which transports cations and anions, respectively. In the figure, the CEMs are red while the AEMs are blue.

Nevertheless, process inefficiencies associated with ED require further minimization. For instance, the migration of ions from the feed to the concentrated stream is not the only transport phenomenon that can occur; other transport phenomena are known to decrease the efficiency of ED, specifically electro-osmosis, back diffusion, and

osmosis.<sup>[29-31]</sup> Electro-osmosis is the migration of water molecules that solvate the ions. Since the ions are transported across the ion-exchange membranes, the water molecules are co-transported

with the ions, thus increasing the effective resistance in the system. As the concentrated compartment accumulates more ions, the concentration gradient between the feed and concentrated compartments increases. The concentration gradient can cause back diffusion, the movement of ions from the concentrated stream into the dilute feed stream.<sup>[25]</sup> Additionally, the greater concentration gradient can also cause osmosis, in which the water molecules transport from the dilute feed into the concentrated stream.<sup>[29]</sup> As the concentration difference increases, the entropic mixing between water molecules and ions becomes more favorable and may take place through back diffusion and osmosis.

ED is a promising pretreatment method that can be integrated with BMED to produce NaOH and HCl at high concentrations.<sup>[7]</sup> In one case, a lab-scale ED system was tested with SWRO brine and optimized in terms of flowrate, applied voltage, and operating mode; as a result, the system had a maximum total dissolved solids (TDS) removal of 98%.<sup>[32]</sup> Nevertheless, lab-scale and large-scale implementations can differ considerably with respect to their optimal operating conditions; thus, identification of the optimal conditions for ED scale-up that maximizes current efficiency and minimizes energy consumption is needed.<sup>[33,34]</sup> A common strategy for scaling up processes is to develop models that characterize the molecular transport phenomena and their corresponding energy usage. Qasem et al. developed a simplified model that took into the consideration of the Donnan potential, the voltage drop at the interface of the membrane and solution, which had significant effects on some design and performance factors.<sup>[35]</sup> Wright et al. compared existing ED models and evaluated how simplifications affected the models' computational time and results.<sup>[36]</sup> Furthermore, they developed an ED model that could predict the desalination rate, limiting current density, and energy consumption.<sup>[36]</sup>

Additionally, further development of membrane materials and surface modifications of membranes can lead to more effective separations of salts from water. By identifying how different materials interact with various ions, membrane materials can be improved to efficiently transfer ions at a low energetic cost. One group has shown the effectiveness of composite membranes prepared with sulfonated polyaniline and sulfonated polyether sulfone, which had a salt removal efficiency of 76.28%.<sup>[37]</sup> Khoiruddin et al. have provided a review of current methods to modify ion-exchange membranes as well as their effects on the performance of the membranes;<sup>[38]</sup> however, a comparative study of the modification methods would be beneficial to determine the optimal route for membrane production.

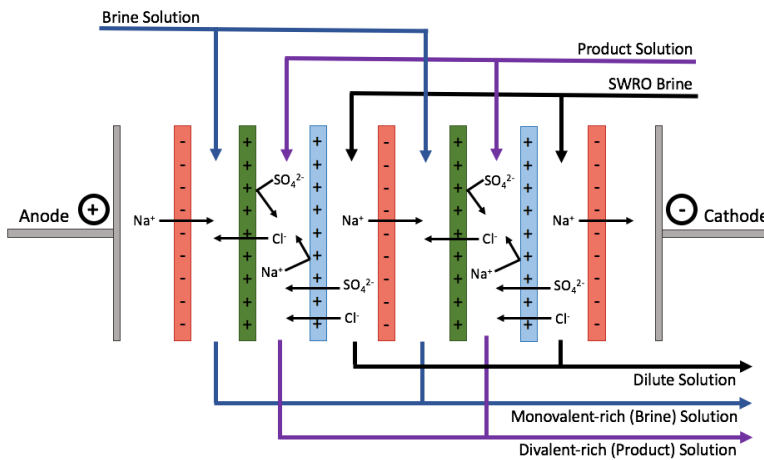
### 2.3. Selective electrodialysis (SED)

Similar to ED, SED is driven by an applied electrical force, which allows for the transport of the ions through charge-selective membranes; however, it can also separate the monovalent and divalent ions in the brine. An SED system is typically composed of an anode, a cathode, anion-exchange membranes (AEMs), cation-exchange membranes (CEMs), and monovalent selective-to-anion (MVA) membranes (Figure 3).<sup>[11,39]</sup> The ions experience an electrical force due to the potential difference between the anode and cathode, causing the anions to move toward the anode while the cations move toward the cathode. CEMs are negatively charged and transport cations and reject anions; on the other hand, AEMs are positively charged and transport anions and reject cations. Since the AEMs and CEMs are generally nonspecific, both divalent and monovalent ions are able to pass through the membranes. Therefore, MVA membranes are added in SED systems to transport monovalent anions while rejecting divalent anions. The alternating sequence of MVA, AEM, and CEM produces monovalent anion-rich, divalent anion-rich, and dilute brine solutions.

By separating the monovalent and divalent anions in the SWRO brine, they can be valorized as different acids through BMED. For instance, a study showed that  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ions could be separated through SED, resulting in NaCl-rich and  $\text{Na}_2\text{SO}_4$ -rich streams.<sup>[14]</sup> After processing the two streams through the BMED system, both streams produced NaOH as the base. Additionally, the NaCl-rich stream produced HCl as the acid while the  $\text{Na}_2\text{SO}_4$ -rich stream produced  $\text{H}_2\text{SO}_4$  as the acid. Current research has explored the technical feasibility of SED by producing MVA membranes through surface modifications and testing the membranes in electrodialysis systems, in which higher permselectivities were observed in comparison to the unmodified membranes.<sup>[11,39-42]</sup> The application of the MVA membranes demonstrated the various methods



of producing the membranes as well as the technology's capability of separating ions based on their valence charge.



**Figure 3.** Schematic drawing of an SED System. SED has monovalent-selective membranes in addition to general CEMs and AEMs. The green membranes are the MVA membranes, which are selective for monovalent anions. The CEMs are red while the AEMs are blue.

In addition to MVA membranes, monovalent selective-to-cation (MVC) membranes can be included to separate monovalent and divalent cations.<sup>[43]</sup> MVC membranes allow the passage of monovalent cations such as Na<sup>+</sup> and reject divalent

cations such as Mg<sup>2+</sup> and Ca<sup>2+</sup>. SED systems with an alternating sequence of CEM, AEM, MVA, and MVC result in the production of separate streams of divalent cations and divalent anions.<sup>[43]</sup> By separating the divalent anions and cations, the formation of molecules that often cause scaling in BMED systems (e.g., CaCO<sub>3</sub> and calcium sulfate (CaSO<sub>4</sub>)) can be prevented. Successful development of MVC membranes has already demonstrated monovalent selectivity for Na<sup>+</sup> ions over Mg<sup>2+</sup> and/or Ca<sup>2+</sup> ions.<sup>[44,45]</sup> For instance, surface-coating of a membrane with polyethyleneimine improved the selectivity for monovalent cations over divalent cations while simultaneously increasing the overall water recovery after RO treatment.<sup>[46]</sup> The application of MVC membranes in electro dialysis systems has also been explored in terms of how the operating conditions, such as conductivity, current density, linear velocity, hydraulic retention time, and stack staging, affect the ion selectivity.<sup>[41,47]</sup> Dotel et al. tested a selective electro dialysis system with different solutions (i.e. a ternary solution, synthetic seawater, and real seawater) at different current densities, which showed that the charge, size, and concentration of the ions had the largest influence on the system's selectivity.<sup>[48]</sup> Furthermore, bench- and pilot-scale electro dialysis systems with MVC membranes were used in the desalination of brackish water, and the two systems had similar desalination behaviour and Na<sup>+</sup> selectivity when operated under the same hydraulic conditions.<sup>[47]</sup> These results show that selective electro dialysis has the potential to be scaled up for industrial use.

Nevertheless, research on SED is relatively new and still requires further investigation, for example in optimizing the operating parameters of SED and determining the characteristics of membrane materials that control the selectivity for monovalent and divalent ions. Furthermore, although SED is promising as a pretreatment technology for water desalination, it also has potential for application in other industries, such as metallurgy,<sup>[49]</sup> agriculture,<sup>[41]</sup> and bioanalysis,<sup>[45]</sup> for separating charged species.

## 2.4. Bipolar membrane electro dialysis (BMED)

After concentrating the brine through NF, SED, or ED, the concentrate can be fed into a BMED system for subsequent acid and base production. NF and SED both remove multivalent ions, but they do not concentrate the brine stream, so the resulting monovalent-rich stream is less able to produce concentrated acids and bases. Conversely, since ED pretreatment can concentrate NaCl up to 200 g/L, the BMED system can produce NaOH and HCl at higher concentrations (approximately 2M).<sup>[13]</sup> By increasing the NaCl concentration prior to BMED treatment, the higher concentration can enhance the performance of the BMED process due to higher ionic conductivity, hence lower ohmic losses. However, one key inefficiency of ED that requires further attention is the removal of multivalent ions from the SWRO brine. As stated before, SWRO brine



contains other ions in addition to Na<sup>+</sup> and Cl<sup>-</sup>; the presence of divalent ions such as Ca<sup>2+</sup> and Mg<sup>2+</sup> can deteriorate the performance of BMED membranes. In order to prevent membrane scaling from calcium and magnesium ions, some authors have proposed the use of monovalent-selective membranes in ED, in which the CEMs are coated with a polymer (e.g., polyaniline) that rejects divalent cations.<sup>[50]</sup> Another solution that has been proven to be successful is the internal integration of SED with BMED, in which the BMED system contains monovalent-selective ion exchange membranes.<sup>[51]</sup> The novel system produced NaOH and HCl with more than 99% purity.

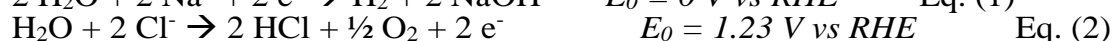
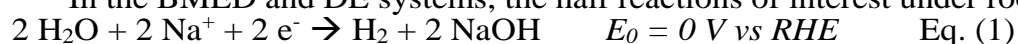
## 2.5. Summary of membrane-based pretreatment processes for brine valorization

Overall, NF, SED, and ED are potential technologies to be integrated with BMED for valorization of desalination brine. Based on the composition of the SWRO brine and the target valorization method, the pretreatment process can be adjusted to deliver the desired BMED product. NF and SED are currently more suited to pretreat brine with divalent ions and avoid membrane scaling. Integration of NF and BMED can provide low concentrations of NaOH and HCl. SED produces separate streams of monovalent and divalent ions, which can be used to produce different acids and bases via BMED. Since ED concentrates the SWRO brine, BMED can subsequently produce NaOH and HCl at high concentrations. For each of the pretreatment technologies, more studies need to investigate their optimal operating parameters and improve membrane materials to maximize process efficiency before they can be used at large scale.<sup>[9]</sup>

## 3. Challenges and opportunities in electrode catalyst materials for more efficient BMED

The energy use of BMED systems has a large influence on their techno-economic feasibility, and the electrode catalyst materials will play a key role in the energy use of BMED systems, particularly depending on their selectivity and their efficiency. In terms of selectivity, unwanted side reactions consume energy, and in extreme cases, they can also require additional separation steps. However, neither of these are major concerns at attainable catalyst selectivities. On the other hand, the catalyst efficiency can have a big impact on the overall energy use, especially for direct electrosynthesis (DE) systems.<sup>[52,53]</sup> Catalyst efficiency and energy use for electrochemical reactions depends on the applied potential, which is the sum of the thermodynamic potential ( $E_0$ ), the overpotential ( $\eta$ ), and the  $iR$  drop ( $E_{iR}$ ). When comparing catalysts, the overpotential is often reported as the overpotential required to achieve a specific current density, typically 10 mA/cm<sup>2</sup> in lab scale tests and above 100 mA/cm<sup>2</sup> for practical applications.

In the BMED and DE systems, the half reactions of interest under room temperature are:



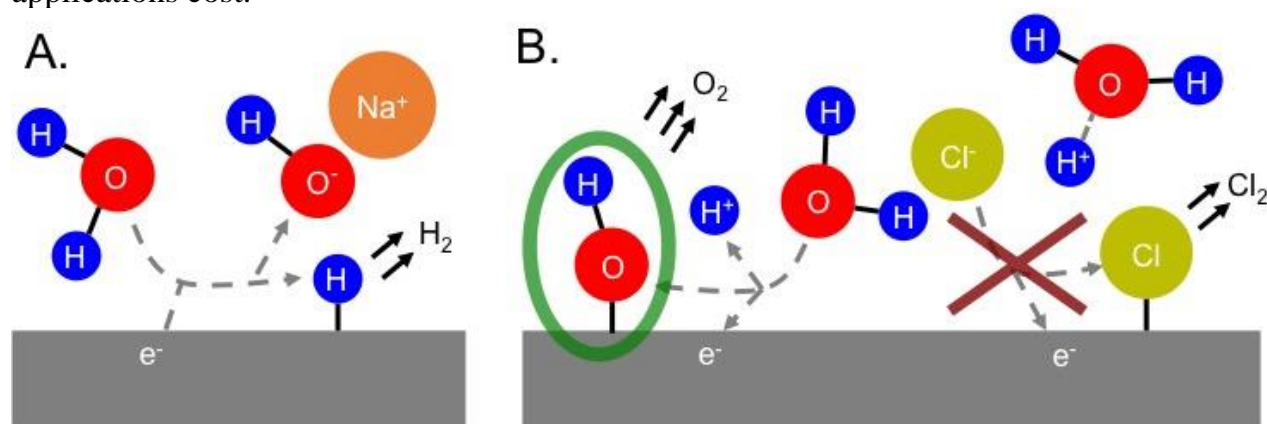
Both BMED and DE process have similar reactions occurring at the electrodes, so similar catalysts can be used, but the energy efficiency of the electrochemical reactions is less influential on the overall energetics of BMED because the electrochemical reactions can be averaged over several parallel streams using several sets of membranes. Thus, having favorable catalysts is particularly important for managing the energetics of DE brine management.

The fundamental reactions described in Equations (1) and (2) have been widely studied in the context of electrochemical hydrogen production from water.<sup>[53]</sup> Indeed, much work has focused on developing new cathode materials and understanding the basic scientific principles for hydrogen production (Equation (1)), ultimately leading to certain catalysts with < 20 mV overpotential for a current density of 10 mA/cm<sup>2</sup>, for example on iridium catalysts.<sup>[54,55]</sup> While further advances in catalyst development could further improve the energetics of the overall system, the existing catalysts are promising if they can be shown to be stable for the long time periods, made of low-cost materials, as well as easily scaled-up for industrial use.

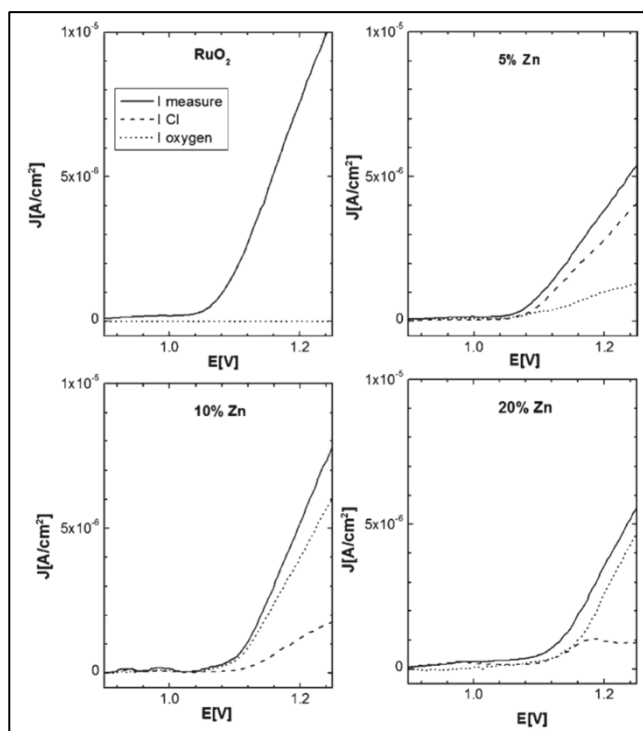
The anodic half reaction (Equation (2)) is likely to be much more energy intensive, with the best oxygen evolution catalysts currently requiring overpotentials in the range of 250 mV to achieve 10 mA/cm<sup>2</sup> in alkaline or acidic conditions.<sup>[39]</sup> Oxidation of water has been widely studied due to its potential use in various energy-related schemes such as hydrogen production, carbon dioxide valorization, or metal-air batteries, but similarities in the intermediates cause scaling

relations in their binding energies that lead to a fundamental limitation of the minimum overpotential required.<sup>[56]</sup>

BMED systems are even more challenging than typical applications of the oxygen evolution reaction (OER), because the reaction must proceed in acidic conditions, and the competing chlorine evolution reaction (CER) must be suppressed, as shown schematically in Figure 4. Chlorine evolution is thermodynamically less favorable than oxygen evolution, but because it is a two-electron process rather than the four electrons required for OER, chlorine production is less kinetically hindered and thus can be more favorable than oxygen production.<sup>[57]</sup> Indeed, CER is typically favored over OER at acidic conditions.<sup>[58]</sup> Catalyst activities for OER and CER were initially found to follow the same trends, where better OER catalysts were also better CER catalysts, but more recent studies have tuned the selectivity of OER over CER by adjusting the catalyst's electronic structure using dopants.<sup>[57,59-61]</sup> Oxygen-selective catalysts in acidic chlorinated conditions are relatively underexplored, yet a few promising early studies have found selectivity for producing oxygen from seawater using doped manganese oxides.<sup>[62,63]</sup> More recent work used similar doped manganese oxides<sup>[52,64]</sup> and other doped oxides<sup>[59,61,65]</sup> to selectively produce oxygen even under acidic brine conditions with reasonable selectivity. For example, based on differential electrochemical mass spectroscopy data, Zn-doped ruthenium oxide shows different OER and CER selectivities depending on the amount of zinc in the catalyst material (Figure 5).<sup>[65]</sup> Additional fundamental work is needed to understand the reaction mechanisms for these catalysts in order to further improve the selectivity and efficiency of OER catalysts in acidic, chlorinated conditions.<sup>[66]</sup> Additionally, catalyst stability will be important for implementation of industrial BMED brine management, so long-term activity studies will be important for assessing new catalysts. In acidic solution, particularly under positive potentials, most of the transition metal oxide materials become unstable and dissolve into the electrolyte. Only a few noble metals including Ir, Ru, Pt, and so on can survive under harsh conditions. How to engineer stable earth-abundant OER or CER catalysts in acid holds the promise for further bringing down the applications cost.



**Figure 4.** Water splitting reactions in a BMED setting. (A) NaOH production from brine will require active catalysts that reduce water to produce hydrogen gas. (B) HCl production from brine will require selective catalysts that produce oxygen gas (via the OH<sub>aq</sub> intermediate shown) selectively over chlorine gas (via the Cl<sub>ads</sub> intermediate shown) under BMED conditions.

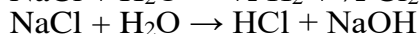


**Figure 5.** Voltammetric (5 mV/s) and differential electrochemical mass spectroscopy of Zn-doped ruthenium oxide catalysts in 0.1 M HClO<sub>4</sub>/0.3 M NaCl electrolyte. For 10% Zn, oxygen is selectively formed over chlorine gas at most potentials (from ref: Petrykin et al.<sup>[65]</sup>).

#### 4. Energy efficiency of BMED

Recently, Thiel et al.<sup>[7]</sup> explored the energy consumption and product formation of four different methods of caustic production by examining their respective thermodynamic limitations. Any brine-to-caustic recycle strategy must produce in-plant usable caustic at a cost equal to or lower than a purchased alternative. Thiel et al. found that these viability factors are largely determined by feed composition, energy usage, concentration of NaOH produced, and purity of NaOH produced. In electrochemical methods, the product formation step is rather straightforward and these methods enable chemical processes with a flexible operational window. The two main chemical pathways

through which NaOH can be produced from brine can be seen in Equations (3) and (4). Equation (3) corresponds to NaOH production from the chlor-alkali process while Equation (4) corresponds to NaOH production from BMED (bipolar membrane electrodialysis) or direct electrosynthesis (DE):



Based on thermodynamic analysis, the theoretical minimum energy requirement for caustic production is 1.56–1.64 kWh<sub>e</sub>/kg NaOH for the chlor-alkali process and between 0.65 and 0.81 kWh<sub>e</sub>/kg NaOH for BMED (these values are based on particular feed and outlet conditions) as reported by Thiel et al.<sup>[7]</sup> Plants using the chlor-alkali process have achieved actual energy usages of as little as 2.1–2.2 kWh<sub>e</sub>/kg NaOH, while test setups using electrodialysis have only achieved 2.3 kWh<sub>e</sub>/kg NaOH (Table 2). The generation of caustic also requires brine purification and concentration prior to the caustic production. Caustic concentration may also need to take place depending on the caustic's intended end use and the process used to create the caustic. Both of these tasks require additional energy, although much less than the caustic production process itself: if the brine and caustic were concentrated to their maximum values, the corresponding thermodynamic minimum energy usage would be 0.06 kWh<sub>e</sub>/kg NaOH for brine concentration and 0.14 kWh<sub>e</sub>/kg NaOH for caustic concentration, which is well below the thermodynamic minima for any of the caustic production processes.

The chlor-alkali membrane process uses 2.10–2.15 kWh<sub>e</sub>/kg NaOH of electrical energy and 0.038–0.047 kWh<sub>e</sub>/kg NaOH of thermal energy (values given on an exergetic basis).<sup>[67,68]</sup> The chlor-alkali diaphragm process tends to have slightly higher electrical energy usage, 1.94–2.51 kWh<sub>e</sub>/kg NaOH, as well as higher thermal energy consumption, 0.128–0.196 kWh<sub>e</sub>/kg (on an exergetic basis).<sup>[67,68]</sup> BMED setups used in research have reported using 1.8–3.6 kWh<sub>e</sub>/kg NaOH of electrical energy.<sup>[30]</sup> BMED processes also produce NaOH at much lower concentrations than the chlor-alkali process. Further, producing more concentrated caustic requires more energy thermodynamically. Thus, while BMED has the potential to require significantly less energy than the chlor-alkali process, more research is necessary to increase its efficiency and lower the realized energy consumption. No study has yet reported on the energy requirements of DE, so further research is needed in this area.

**Table 2.** Required energy for caustic production process.

Process for Caustic Production	Chlor-alkali Membrane	Chlor-alkali Diaphragm	Bipolar Membrane Electrodialysis	Direct Electrosynthesis
Theoretical Min. Energy Required (kWh/kg NaOH)	1.56–1.64 <sup>[7]</sup>	1.56–1.64 <sup>[7]</sup>	0.65 and 0.81 <sup>[7]</sup>	0.65 and 0.81 <sup>[7]</sup>
Experimentally Realized Energy Usage (kWh/kg NaOH)	Electrical: 2.10–2.15 <sup>[67,68]</sup> Heat** <sup>†</sup> : 0.038–0.047 <sup>[67,68]</sup>	Electrical: 1.94–2.51 <sup>[67,68]</sup> Heat** <sup>†</sup> : 0.128–0.196 <sup>[67,68]</sup>	1.8–3.6 <sup>[67]</sup>	*n.a.

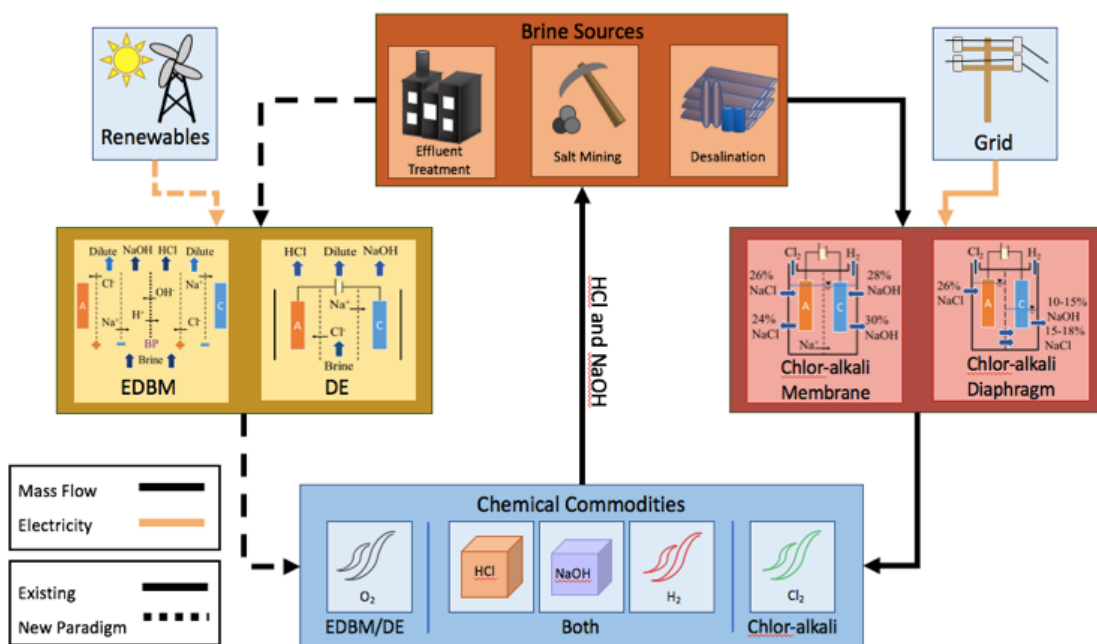
\*n.a. not enough information or data available, indicates areas where more research is needed.  
<sup>†</sup>\*\*Thermal energy values are stated on an exergetic basis.

## 5. Feasibility and product usage

The maximum producible NaOH is about 18.1 g/kg-seawater [primarily limited by the Na<sup>+</sup> ions availability in the seawater], while typical plants use orders of magnitude less [NaOH producible from 0.002 – 0.01% of total concentrate flow.<sup>[7]</sup> Furthermore, various chlorine-based byproducts can be used within the desalination plant. For example, CaOCl<sub>2</sub>, Cl<sub>2</sub>, NaOCl are used for chlorination, and HCl is used for cleaning.<sup>[7]</sup>

## 6. Outlook: Coupling the water, chemical, and renewable energy industries

In the proposed paradigm, electrochemical systems would take in desalination brine and operate with electricity from a renewable power source (Figure 6). Solar powered electrodialysis for desalination has been studied for some time.<sup>[69-71]</sup> Today, membrane desalination by renewable sources, including solar and wind power, is feasible at both small and large scale.<sup>[72, 73]</sup> Further, thermal desalination by solar power has potential, often with integrated energy storage.<sup>[73]</sup> Because the onsite demand for NaOH is below the production potential of a given plant, caustic-recovery could be driven with intermittent energy sources, such as wind and solar.<sup>[74]</sup> Some recent studies also suggest that renewable energy sources have the potential to provide more sustainable and economical energy to drive membrane-based desalination processes,<sup>[75-77]</sup> especially in consideration of new developments in the renewable energy sector.<sup>[76]</sup> Recently, Kim et al. showed an excellent example of solar-based desalination.<sup>[78]</sup> As a result, the production of NaOH could become more economically viable on a cost per energy basis. Onsite production of NaOH would also reduce the energy demand and hazards involved in chemical transportation. To summarize, the system produces chemicals such as NaOH and HCl and provides a possibility of fluidity and interconnectedness among the water, renewable energy, and chemical industries. Recovery of caustic from desalination brine also aligns with the current trend toward resource recovery and a circular economy, and this approach can reduce inefficiencies and risks associated with transportation, storage, and distribution of chemicals.



**Figure 6.** Current and envisioned interconnectedness of the water, chemical and renewable energy industries. This futuristic integration is notional and its feasibility would need to be explored. Black lines indicate mass flow and orange lines indicate electrical energy transport. Possible incorporation of interconnectedness is shown by dashed lines, and solid lines indicate the current state. Rather than releasing brine back into the ocean, seawater desalination plants may instead recycle brine, simultaneously producing fresh water, NaOH, and HCl. NaOH could be directly used in the desalination process to replace external sources. Chlorine byproducts, such as HCl, could be used either within the plant or marketed; and H<sub>2</sub> gas can potentially be used as an energy source. In addition to the incorporation of renewable energy, NaOH and HCl production has a lower thermodynamic minimum energy than the standard-bearing chlor-alkali process, and chemical transportation would be reduced. Seawater desalination plants would realize increased overall sustainability and economic benefits as well.

## 7. Summary and future directions

We propose that NaOH production is a viable strategy for onsite brine valorization, recognizing that further process modelling and electrode material development is needed for the technology to realize its full potential. Recent thermodynamic limits analyses<sup>[7,9]</sup> and the above discussion focus on the energy requirements for caustic production, which are promising compared to the incumbent chlor-alkali process. Future research needed before this approach can be scaled up is summarized in Box 1.

### Box 1. Future research directions

1. Further improvements to the energetics and selectivity of membranes for brine pretreatment.
2. Improved catalyst selectivity (for oxygen production over chlorine production) and long-term stability.
3. Technoeconomic assessment of BMED and caustic production.
4. Potential for renewable energy to drive plants with integrated caustic recovery.

Briefly, although the brine pre-treatment processes could be improved, the main areas in which future research should focus are technical improvements to and techno-economic analysis of the BMED process, especially work toward improved catalysts. The potential for coupling to intermittent renewables should also be explored in the context of the entire plant. Advances in these areas may eventually position caustic recovery as an energy-efficient, cost-lowering, and environmentally friendly component of all major desalination plants.

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