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Ocean Alkalinity Enhancement Using Bipolar Membrane Electrodialysis: Technical Analysis and Cost Breakdown of a Full-Scale Plant

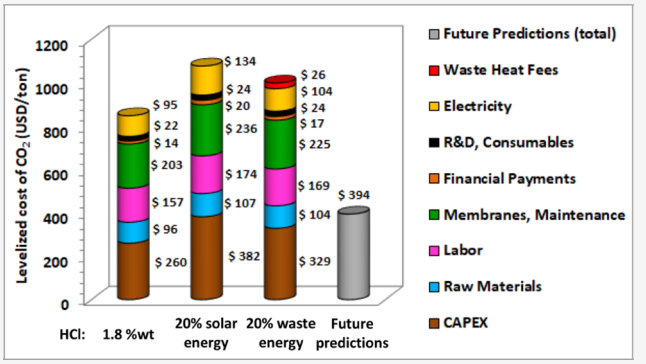
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ABSTRACT: A detailed techno-economic analysis was performed for a bipolar membrane electrodialysis (BMED) full-scale plant designed to produce large volumes of dilute alkaline solution for use in ocean alkalinity enhancement (OAE). OAE is a process by which the surface of the oceans is realkalinized to promote CO_2 absorption from air by converting CO_2 to carbonates for long-term storage in the oceans. The capacity of the BMED stack was designed to process ~139 000 m^3/year of desalination brine, resulting in 47 200 t/year of 2.1 wt % NaOH solution. The OAE plant was modeled using colocation with a desalination plant in southern California. Three scenarios were investigated, each focused on a different valorization of the BMED process byproduct of 46 600 t/year of 1.8 wt % HCl solution: selling (1) dilute HCl without further processing, (2) dilute HCl distilled to 20 wt % using carbon-free (solar) energy, and (3) dilute HCl distilled to 20 wt % using waste heat from a nearby power plant. The levelized cost of CO_2 sequestration from the OAE plant, assuming no return on investment, ranged from 848 to 1076 USD/t of CO_2, depending on the scenario. Subsequently, a discounted cash flow analysis was conducted to assess the price at which carbon credits would have to be sold as revenue source to make a profit on the plant. Our analysis indicates that the cost of energy, labor, loan repayment, and membrane replacement, as well as the inefficiency of commercial membranes, drive the economics of BMED for OAE, while highlighting the necessity to generate alternative byproducts other than HCl. Nevertheless, these high costs (1395−2315 USD/t of CO_2) align with carbon credit prices currently indicated in contracts signed within the voluntary carbon market. A reliable outlook indicates that technical improvements and better economic perspectives can reduce the levelized cost of CO_2 down to 394 USD/t of CO_2.



1. INTRODUCTION

As per the Paris Agreement, it is desired to keep global temperature rise by 2100 to well below 2 °C above preindustrial levels. To achieve this, it is necessary to both reduce greenhouse gas emissions and remove excess carbon dioxide from the atmosphere. An estimated 100−1000 Gtons of CO_2 removal is required to meet the 1.5 °C target, estimated at 10−15 Gtons of CO_2 removal each year starting from 2040.[1] Ocean alkalinity enhancement (OAE) is one of several technological approaches that has the potential to massively reduce atmospheric carbon concentrations, but such an approach must be thoroughly evaluated for its techno-economic feasibility to assess whether it is a viable path forward.

Several carbon dioxide removal strategies are actively being researched and implemented by start-ups. The most viable approaches include direct air capture (DAC) whereby CO_2 from the air is absorbed, concentrated, and either stored and/or used,[2] bioenergy with CO_2 capture and storage (BECCS) whereby vegetation is grown to remove CO_2 from the atmosphere, then burned to produce energy with the emitted CO_2 captured, concentrated, stored and/or used,[3] soil nutrient seeding whereby nutrients are added to soil to increase carbon sequestration,[4] and marine carbon dioxide removal (mCDR)[5] which includes methods such as OAE whereby alkaline material is added to the ocean's surface to increase the adsorption of CO_2 from the atmosphere to the oceans.[6] OAE has several distinct advantages over these other approaches: the oceans are the largest carbon sink in the world, covering approximately 71% of Earth's surface and absorbing approx-

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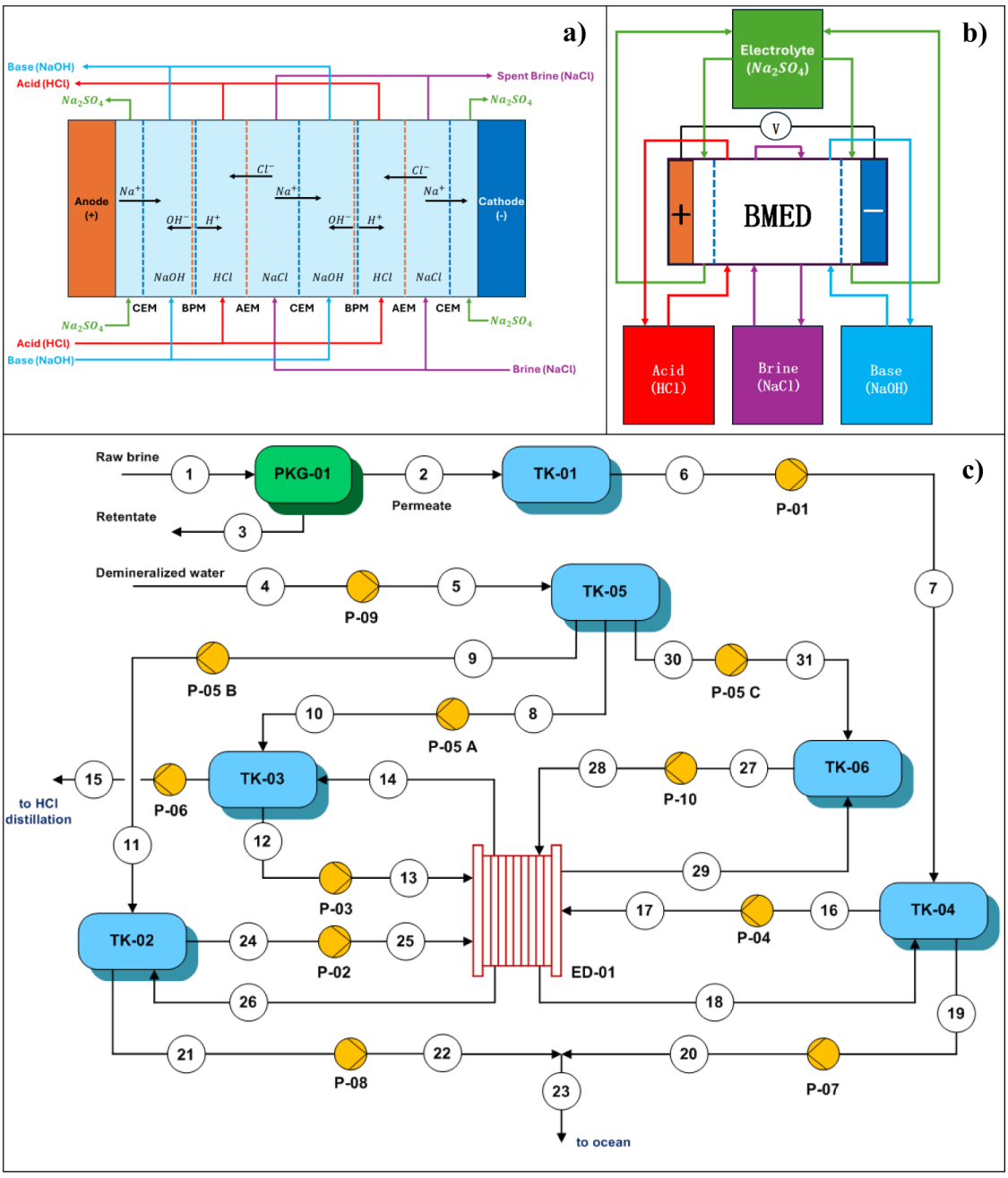


Figure 1. (a) Bipolar membrane electrodialysis (BMED) membrane module schematic with NaCl as the feed solution and NaOH and HCl as byproducts. CEM, AEM and BPM are the cation exchange membranes, anion exchange membranes, and bipolar membranes, respectively. (b) BMED Batch/Closed-loop configuration. (c) Flow diagram of the OAE process (unit operations are PKG-01: nanofiltration (NF) package; TK-01, ... −06: mixing tanks; *p*-01... −10: pumps; ED-01: electrodialysis stack). Each of the numbered circles represent the streams to or from these unit operations.

imately 30% of all CO_2 emissions,[7,8] the capacity for the oceans to absorb CO_2 is several orders of magnitude greater than the amount of CO_2 that must be removed, and CO_2 is stable in the oceans for more than 10 000 years.

When CO_2 dissolves in the oceans, it enters the carbonate cycle, causing carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions to accumulate. Due to the pK_a of the $H_2CO_3/HCO_3^-/CO_3^{2-}$buffer system, as CO_2 dissolves in the oceans, more protons (H^+) dissociate in solution to create carbonic acid (H_2CO_3), thus decreasing oceanic pH.[9] In addition to the negative impacts of ocean acidification on the entire biosphere, the shifting of this equilibrium toward carbonic acid also inhibits the absorption of additional CO_2.[9] Adding alkaline species to the surface of the ocean can counter ocean acidification and reverse this equilibrium enhancing CO_2 absorption. OAE is scalable and simple as it is not tied to complex biological processes and studies have shown that it is among the most efficient methods for countering ocean acidification and enhancing CO_2 absorption due to its chemical simplicity and effectiveness in shifting the carbonate equilibrium.[10−12]

Theoretically the most efficient way to produce alkaline species is through bipolar membrane electrodialysis (BMED).[13] BMED can convert saltwater into acid and base.

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A strong electric field separates abundant sodium chloride (NaCl) into its constituent ions which are kept separate by anion and cation exchange membranes. Simultaneously, bipolar membranes dissociate water into OH^- and H^+, which combine with the separated Na^+ and Cl^-, respectively to produce dilute sodium hydroxide (NaOH) and hydrochloric acid (HCl).[7] The produced dilute NaOH can be added to the oceans to gently adjust its pH. Several versions of this technology have been developed,[14] validated, and assessed for their techno-economic feasibility.[15] The simplest approach described above has been proposed and demonstrated, and ongoing research seeks to optimize BMED operational parameters including enhancing water dissociation in bipolar membranes (BPMs),[7] managing membrane fouling,[16] or optimizing operating parameters such as flow rates. However, no full techno-economic analysis has been performed to assess its large-scale feasibility. No previous reports have realistically considered the costs associated with the byproduct dilute hydrochloric acid that is produced in large volumes. The present paper represents the first detailed study that investigates the investment and operating costs of a full-scale OAE plant producing dilute NaOH and HCl. The plant's capacity and technology are assumed to be developed at Technology Readiness Level (TRL) 7, i.e., a system prototype demonstration in operational environment. The performance of the stack, which is the core of the plant, is based on experimental data obtained from a commercial BMED unit using commercially available membranes operated in the lab. The average electrical consumption was calculated based on the power and operating hours, even though it is recognized that consumption varies over time due to fluctuations in voltage and current. These changes are influenced by factors such as conductivity and mass transfer limitations and ideally would be integrated over time. Importantly, the equipment purchase costs were estimated by direct quotations.

2. DESCRIPTION OF THE PLANT

The plant is based on a bipolar membrane electrodialysis (BMED) system that treats brine generated from a desalination plant.[14,17] The analysis in this paper is based on experimental data from a lab-scale setup, which was used to scale up to the size of the plant. BMED is a process that converts seawater into acid and base under a strong electric field generated across two Ti−Pt electrodes positioned at the ends of a series of membranes (the stack). A set of three membranes is known as a triplet, and consists of a bipolar membrane (BPM), an anion exchange membrane (AEM), and a cation exchange membrane (CEM). AEMs and CEMs are indicated by + and − symbols in Figure 1a, respectively. A bipolar membrane (BP in Figure 1) is an AEM bound to a CEM (sometimes containing a catalyst layer between them), with a water interface in between.

Within each BMED triplet, there are three distinct channels for acid, base, and salt, which are kept separate by the BPM, AEM, and CEM. Under the applied potential, protons produced from the dissociation of water inside the BPM, and chloride ions from the salt channel migrate to the acid channel to form hydrochloric acid (HCl), while hydroxide ions produced from the dissociation of water on the other side of the BPM and sodium ions from the salt channel, move to the base channel to produce sodium hydroxide (NaOH). A sodium sulfate (Na_2SO_4) electrolyte, also called an electrode rinse solution (ERS) is circulated through the channels at the electrodes to allow for the exchange of sodium ions across the outermost CEMs, and to prevent the diffusion of unwanted protons or chloride ions (Cl^-) to the electrodes, where they would be electrochemically converted to hydrogen (H_2) and chlorine (Cl_2) gas. The experimental BMED system included three membrane triplets (AEM-CEM-BPM) with an area of 192 cm^2, and an applied voltage of 30 V. This system was extrapolated to the full-scale plant size to calculate the required membrane area and the number of modules. Table 1 provides a summary of the extrapolated plant data. Detailed experimental data can be found in the Supporting Information.

Table 1. Technical Process Parameters of the Full-Scale Stack ED-01 That Aligns with the Liquid Flow Rates from a Full-Scale Desalination Plant, Such as Carlsbad, CA

	Acid chamber, HCl 1.8 wt %	Brine chamber, Brine	Base chamber, NaOH 2.1 wt %	ERS, 20 wt % Na
Tank volume (m^3)	28	84	28	12
Pump recirculation flow-rate (m^3/h)	56	56	56	56
Product (m^3/day) [t/year]	140 [46 662]	420 [166 320]	140 [47 216]	-
Electrode material	Ti−Pt alloy	-	Ti−Pt alloy	-
Total membrane area (m^2)	922			
No. of triplets	50			
No. of modules	1600			

The modeled plant operates in a closed loop configuration (CL), using desalination brine as saltwater feed. All solutions, i.e., HCl, NaOH and brine, as well as Na_2SO_4 are recirculated until the NaOH solution reaches the desired concentration (Figure 1b).[18] Hence, the plant is designed to work in a batch operating mode and its daily capacity is established by the size of the stack.

Brine was selected due to its higher NaCl concentration (1.3 M) compared to seawater (~0.6 M), which facilitates a higher concentration in the final products, i.e., NaOH and HCl. After 3.5 h of operation, the NaOH and HCl solutions reach a final concentration of approximately 2.1 and 1.8 wt %, corresponding to 0.54 and 0.49 mol/L, respectively.

The block diagram is shown in Figure 1c, whereas the detailed process flow diagram (PFD) of the plant is shown in Figure S.0, where the most significant control loops are indicated.

The brine stream coming from the reverse osmosis (RO) module of an upstream desalination plant (not indicated in Figures 1 and S.0) undergoes pretreatment stage by a two-stage nanofiltration (NF) unit: NF membranes are necessary to reduce the concentration of calcium and magnesium to approximately 10 mg/L. This threshold is pivotal to prevent mineral scale formation on the BPMs, AEMs, and CEMs. Unfortunately, some Na^+ and Cl^- ions are also removed by the NF unit.

The flow rate (stream 1 in Figure 1c) of the feed brine is 100 m^3/h, whereas the permeate recovered downstream of the NF is 70 m^3/h (2). This pretreated brine is stored in a 500 m^3 tank (TK-01), whereas the NF retentate (3) is directed to the outfall and discharged into the ocean. All plant controls (e.g., level controllers), safety considerations, and minor processes are detailed in the SI.

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The BMED plant needs deionized water (DIW), which is diverted from the permeate flow of the desalination plant, which is an insignificant fraction of the daily water produced by an average facility.

Pumps *p*-05 A/B/C fill tanks TK-02 (35 m^3), TK-03 (35 m^3) and TK-06 (20 m^3) with 28, 28, and 12 m^3 of DIW, respectively. A flow controller and totalizer switch off *p*-01 once 84 m^3 of brine have filled the downstream tank TK-04.

In the mechanically mixed tank TK-06 powdered sodium sulfate is added to water to obtain a 200 g/L solution of Na_2SO_4 (electrode rinse solution)[18] to reduce hydrogen, oxygen, and chlorine gas evolution next to the electrodes, which reduces product efficiency. Filling these four tanks takes 30 min, and the flow rate of the four pumps was chosen accordingly.

The 3:1:1 volume ratio for brine:HCl:NaOH solutions was selected according to trials carried out with a pilot-scale in Italy.[18] Nevertheless, a suitable brine:HCl:NaOH ratio ranges from 3:1:1 to 2:1:1, according to our experiments and indications from a leading international company, but other authors have suggested 4:1:1 or 5:1:1.[19] The higher ratio generates a higher NaOH concentration for the same process time.[19]

DIW from tanks TK-02 and TK-03, brine from TK-04 and sodium sulfate from TK-06 are continuously recirculated through stack ED-01 by pumps *p*-02, *p*-03, *p*-04 and *p*-10 in a closed loop configuration. pH, conductivity, temperature, and pressure are measured upstream and downstream of the stack, i.e., in streams 13−14, 17−18 and 25−26. Sodium sulfate solution is not consumed. Nevertheless, a little makeup is required occasionally because of evaporation. pH and conductivity are only measured in TK-06. The batch cycle operates for 3.5 h. During this time, the DIW flowing through the cathodic side increases its concentration in NaOH, whereas the anodic solution becomes more concentrated in HCl. Contemporaneously, the NaCl concentration in the brine stream decreases. At the end of this cycle, the set-point of NaOH (2.1 wt %) is reached, all tanks are drained, and the process is restarted.

Membranes, connections, controls devices, current generator and electrodes are supplied by a vendor and all equipment are included in the stack package (PKG-05).

When the solution in TK-02 reached 2.1 wt % concentration, the AC controller stops pumps *p*-02, *p*-03, *p*-04 and *p*-10, as well as the current generator of stack ED-01. Once the NaOH set-point (2.1 wt %) is reached, pumps *p*-07 and *p*-08 deliver the spent brine and the diluted NaOH solution into the ocean by a 1.5 km-long Φ8 pipeline (stream n.23) with a raiser of 40 m, which releases the solution to the surface of the water. Spent brine is reduced in its concentration from 1.3 M down to 1.14 M which could be partially recycled to the inlet of RO membranes at the desalination plant or released back to the ocean but with fewer restrictions on coastal release. The intermittent release of the alkaline solution is preferred as it can be spread more efficiently by waves and marine currents, avoiding accumulation around the raiser. Moreover, the spent brine further dilutes the alkaline solution.

Pump *p*-06 transfers the 1.8 wt % HCl solution into a buffer tank, which either feeds a distillation plant or is shipped offsite. Package PKG-06 (not reported in the PFD) includes a tank, heat exchanger, distillation column, reboiler and condenser, made up of stainless steel (SS) lined with glass. From the buffer tank, the HCl solution continuously feeds the distillation column (24 h per day, 7 days per week) where acid is concentrated to approximately 20 wt %, i.e., below the azeotropic concentration of 20.2 wt %. The full package would be supplied by a vendor with expertise in HCl distillation plants and would contain one boiler and chiller for HCl distillation, and a diesel generator with the relevant tank for fuel storage in case of emergency.

TK-02, TK-03, and TK-04 are not completely emptied at the end of the cycle. To avoid triggering the low-level alarm few m^3 of NaOH and HCl solutions remain in the tanks to which fresh DIW is added. As such, at the start of each BMED cycle (excluding the first cycle), the NaOH and HCl compartments contain low levels of NaOH and HCl slightly reducing the ion gradient across the CEM and AEM membranes, respectively, but providing sufficient ion conductivity to reduce electrical resistance across these compartments. At plant start-up only, some NaOH and HCl must be added to DIW in TK-02 and TK-03 for sufficient solution conductivity.

The total duration of a batch cycle is 4.5 h (BMED lasts 3.5 h, filling TK-02, TK-03, and TK-04 lasts 0.5 h, and emptying them lasts 0.5 h), thus, 5 cycles can be conducted in 1 day. The plant works 330 days/year, to account for holidays, normal, and extra maintenance. The plant can thus produce 140 m^3/day (28 m^3/batch • 5 batches) of NaOH and HCl solutions. A section of the plant is dedicated for utilities processing, in particular air compression, dehydration, and deoiling. Devices for safety include a firefighting system with one electric and one diesel pump, while water in TK-05 will be used by the pump in case of emergency.

3. ECONOMIC ANALYSIS

Coupling BMED with desalination plants has previously been identified as one of the most cost-effective synergies, as desalination plants provide pretreated high brine concentrations as feed to the BMED system, while also offering existing intake and outfall infrastructure to help reduce capital investment and energy consumption.[14] Nevertheless, some costs from the desalination plant will be incurred including the deionized water required to fill the acid and base compartments: such water is the permeate from the desalination plant before remineralization.

We have based our plant on the production capacity of the Carlsbad plant in California, USA. The total annual volume of brine used in our plant (138 600 m^3/year) is less than the daily production of sweet water of a full-scale plant (190 000 m^3/day), and whose remineralized water production cost is $0.005 USD per gallon.[20] We have included the following assumptions in our techno-economic model:

- Operation: 330 days/year and 22.5 h/day.
  The plant runs in closed loop configuration.
- Labour cost: personnel are reduced to a minimum of 3 specialized workers and 1 manager.
  It is a fully automated and remotely controlled plant, so the personnel can be reduced to a minimum while also avoiding the costs of night shifts. One worker is for the BMED system, one is for the NF system, one is for the remainder of the equipment, and the manager overseas the entire plant's operation, worker schedules, admin, etc. We have not included a technical director, admin staff, or maintenance workers to minimize costs.
- Plant lifetime: 20 years.

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- Membrane replacement rate: 3 years.
  Membrane replacement rate was estimated from our experiments and the literature.[19] At this replacement frequency, 6 membrane changes will be needed over the lifetime of the plant.
- Tax rates: 29.84%.
  In US, the total tax rate is the sum of the federal corporate tax, which is 21% of taxable income, and the specific state corporate tax, which is 8.84% in California.[21−23]
- Interest rates: 4.25%.
  This is the current average interest rate for business mortgages, provided by US banks for a 10-year repayment period.[24]
- Moles of CO_2 captured for every mole of NaOH: 0.8.
  This is based on a review of the literature and recent estimates.[25]
- Measurement, Reporting, and Verification (MRV): We did not consider MRV in our model.
  MRV refers to measuring, reporting, and verifying the carbon dioxide removals achieved by a project. MRV associated costs can vary significantly, and this is still a nascent field, making it difficult to properly estimate. MRV is crucial for validating the effectiveness of carbon removal projects and ensuring compliance with regulatory standards. The variability in MRV costs arises from factors such as the complexity of the technology employed, the scale of the project, and the specific requirements of regulatory bodies or certification standards.

These parameters can be varied in our model to identify cost limits and sensitivities, and to adapt to various tax and interest rate environments. The present values were chosen for realism in the current presentation.

The economic analysis was performed following the approach in Peters et al.[26] and successfully used in other profitability analyses carried out to evaluate innovative chemical-environmental processes.[15,27−29] This approach leads to a very detailed estimation of the Capital Expenditure (CAPEX) and Operating Expenditure (OPEX), with an accuracy in the range ±10−15%. Details of materials selection can be found in the SI.

An ideal location for the plant could be the area of the Carlsbad desalination plant, located on the seashore of the city of Carlsbad, CA, (USA), 55 km north of San Diego. In addition, in the same area there is one 500 MW power plant, equipped with five gas turbines. The power plant's flue gas and cooling water can supply the thermal and cooling energies required for the distillation of HCl. There are several open fields next to the desalination plant and near the power plant, making this a realistic site for the construction of an OAE plant. Other locations worldwide match these conditions, including in Qatar, United Arab Emirates, and Australia.

The plant generates 140 m^3/day of 2.1 wt % NaOH solution, i.e., approximately 47 200 t/year, that corresponds to 998 t/year of 100% NaOH.

The adsorption capacity of alkalinized seawater can be provided as an average value; the phenomenon is complex and influenced by several factors including salinity, surface water temperature, wave mixing, ocean currents, and wind. The absorption kinetics is slower than simple absorption in a column with alkaline solution, and some authors have tried to mathematically model and quantify the CO_2 uptake.[30,31] As a preliminary estimation of the uptake, it was considered that each mole of NaOH discharged into the sea absorbs 0.8 mol of CO_2 (assuming solid pellets of 100% NaOH not in solution).[25] Hence, the total expected removal of CO_2 is 878 t/year (calculated as 998 t 100% NaOH/year × (44 g/mol CO_2/40 g/mol NaOH) × 0.8 mol CO_2/mol NaOH). This is the value used to claim the carbon credits generated by the plant.

In addition, 140 m^3/day of 1.8 wt % HCl solution (46,662 t/year) are also produced: unlike alkaline solution and spent brine, hydrochloric acid cannot be released into the ocean but has previously been suggested to be a salable byproduct to support plant revenue.[18] Hence, three different techno-economic scenarios were investigated considering the post-processing of the HCl byproduct:

Scenario 1: direct sale of 1.8 wt % HCl solution

Scenario 2: distillation of HCl to 20 wt % commercial grade using carbon neutral energy

Scenario 3: distillation of HCl to 20 wt % commercial grade using waste heat from a local power plant

Table 1 reports the technical parameters of the stack common to all scenarios.

3.1. CAPEX Estimation. The energy and material (E&M) balance from the process flow diagram (PFD) was used to design the main equipment, determining necessary volumes, flow rates, and energy requirements. Equipment costs were based on quotes from manufacturers, except for the BMED stack, which required extrapolation from a smaller capacity quote. The Equipment Purchase Cost (EPC) excludes delivery, installation, taxes, and insurance but includes utility and emergency equipment and a 2% factor for unaccounted-minor components.

Additional CAPEX considerations include transportation, import tariffs, land purchase, yard improvements, laboratory equipment, installation, piping, instrumentation, insulation, electrical work, and the different buildings required. These costs represent the Total Plant Direct Cost (TPDC). The Total Plant Indirect Cost (TPIC) includes engineering, procurement, construction, labor and material, supervision, start-up, training, and contingencies. The sum of TPDC and TPIC results in the Direct Fixed Capital (DFC).[32] The detailed CAPEX breakdown is provided in the Supporting Information.

3.2. OPEX Estimation. The OPEX estimation includes all annual expenses required to operate the plant, including raw materials, labor, laboratory and quality assurance costs, consumables, waste treatment and disposal, utilities, running royalties, facility-dependent items, loan payments, and miscellaneous costs. Of note, loan payments are evaluated separately, with OPEX divided into financial OPEX (initial CAPEX investment plus interest) and technical OPEX (plant operation costs), averaging over 20 years with a 1.5% annual inflation rate. All other OPEX details are presented in the SI.

3.3. Economic Evaluation Report. The Economic Evaluation Report (EER) outlines several key financial aspects: Direct Fixed Capital (DFC), working capital (funds reserved for operating expenses like labor, raw materials, utilities, waste treatment, and miscellaneous costs), start-up and validation costs (expenses related to achieving full operational capacity), and up-front R&D costs (research expenses for process optimization before manufacturing). No up-front royalties were considered since no external patents are used. The total

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investment is the sum of DFC, working capital, start-up costs, and upfront R&D.

The plant's revenue is generated from the sale of HCl, whether diluted or concentrated, and its cost was adjusted annually at a 1.5% inflation rate. The minimum carbon credit revenue was calculated to identify the breakeven point, i.e., the price of carbon required to make the total revenues equal to total OPEX (technical plus financial, the latter considering the annual share of CAPEX to be repaid). The breakeven point was also calculated considering a discounted cash flow corresponding to an opportunity cost of capital of 2%, 5% and 7%. In each of these "opportunity cost of capital" scenarios, the required price of carbon credits was calculated to achieve different profit scenarios.

Importantly, economic indicators like gross margin, return on investment (ROI), and payback time were not calculated because the gross profit, defined as revenues minus total operating costs, is consistently negative.

3.4. Discounted Cash Flow Analysis. After determining the unit consumption of the OAE process, the analysis was expanded to include carbon credits. Carbon credit management varies by country, which can be sold on the Emission Trading System (ETS), and the Voluntary Carbon Market (VCM). These carbon credits can also be used for taking advantage of current tax benefits in the US where this plant was modeled. In this paper, the specific value of tax credits was not included in the calculations due to their variability across countries and ongoing changes in policies. Instead, the analysis focused on determining the required cost per metric tonne of CO_2 removed.

A cash flow analysis was conducted for three scenarios using the Discounted Cash Flow (DCF) method, which accounts for the time value of money over a project's lifetime. Key indicators include Net Present Value (NPV), Profitability Index (PI), Discounted Payback Time (DPBT), and Internal Rate of Return (IRR). The IRR indicates the interest rate at which the project's NPV is zero.[26,27] These indexes are calculated as follows:

Net present value (NPV)

$$NPV = \sum_{k=0}^{N} \frac{CF_k}{(1+r)^k} \tag{1}$$

Profitability Index (PI)

$$PI = \frac{NPV}{Total\ Investment} \tag{2}$$

where r is the opportunity cost of capital (%), CF_k is the net cash flow in year k, and N is the project lifetime (years).

The IRR is the discount rate that makes the NPV of a project zero. In other words, it is the expected compound annual rate of return that will be earned on a project or investment:

Internal Rate of Return (IRR) for which Net Present Value (NPV) is zero

$$NPV = \sum_{k=0}^{n} \frac{CF_k}{(1+IRR)^k} = 0 \tag{3}$$

The DPBT corresponds to the time needed for a project to generate enough cash flows to break even and become profitable, namely, when the sum of the discounted cash flows becomes positive:

Discounted Payback time (DPBT) to break even on the project

$$\sum_{k=0}^{DPBT} \frac{CF_k}{(1+r)^N} = 0 \tag{4}$$

The analysis adjusted the carbon credit value to achieve a PI equal to 1.03, considering various opportunity costs of capital, ranging from 2% to 7%, to reflect different investment risks.

Depreciation, reflecting the gradual decline in the value of physical facilities over time, was also included in the DCF analysis. Depreciation was calculated using the straight-line method over a 10-year recovery period, appropriate for a chemical plant.[26] The salvage value of the facility after this period was assumed to be zero.

4. ANALYSIS OF THE SCENARIOS

Each of the three scenarios is described in the following section. The most significant economic parameters are discussed, highlighting the differences among them.

For all three scenarios, the greatest contributions to OPEX as shown in Figure 2 are (1) the facilities operations, which is dominated by membrane replacement costs, (2) labor costs, and either (3) raw materials consumption, which is dominated by the cost of using deionized water (DIW), and 4) energy consumption.

Other minor OPEX are the same across all three scenarios such as laboratory activity, quality control (QC), maintenance, insurance and local taxes, consumables and other costs including marketing. We assumed that membranes are replaced every 3 years, estimated from our experimental work on a large lab-based BMED system and confirmed by other researchers.[19] This replacement cost was amortized over the plant lifetime and dominates the facility-dependent costs.

For all three scenarios, the greatest contributions to CAPEX as shown in Figure 2 are (1) the BMED stack, (2) the nanofiltration module, and (3) the distillation columns (Scenario 2 and 3). The equipment purchase costs (EPC) in 2024 are considerably higher than in the past 10 years due to various economic conditions (e.g., inflation, higher interest rates, increased energy costs) and remain uncertain. The current model assumes current interest rates (~4.25%), which are higher than the past 20 years, but historically moderate. Of note, equipment such as the BMED stack can only be purchased from a limited number of manufacturers worldwide, unlike most other common devices (e.g., pumps, tanks, NF modules, and pipes) that are widely available globally. High shipping and transportation costs as well as increasing import tariffs must be considered as these can quickly erode savings from purchasing equipment from low-cost manufacturing countries.

4.1. Scenario 1: Direct Sale of the 1.8 wt % HCl Solution. This scenario investigates the direct sale of acid to buyers which could use the diluted solution as-is for their processes, for instance for use as cleaning solution, directly in manufacturing, or to produce concentrated acid or other chlorine-based products. Ideally, the use of the dilute acid is close to the BMED plant, so that the dilute HCl could be delivered through a short pipeline, avoiding transportation costs and the associated CO_2 emissions. EPC for this simplest, and admittedly least realistic scenario, contains all primary components of the plant as detailed in Figure 1.

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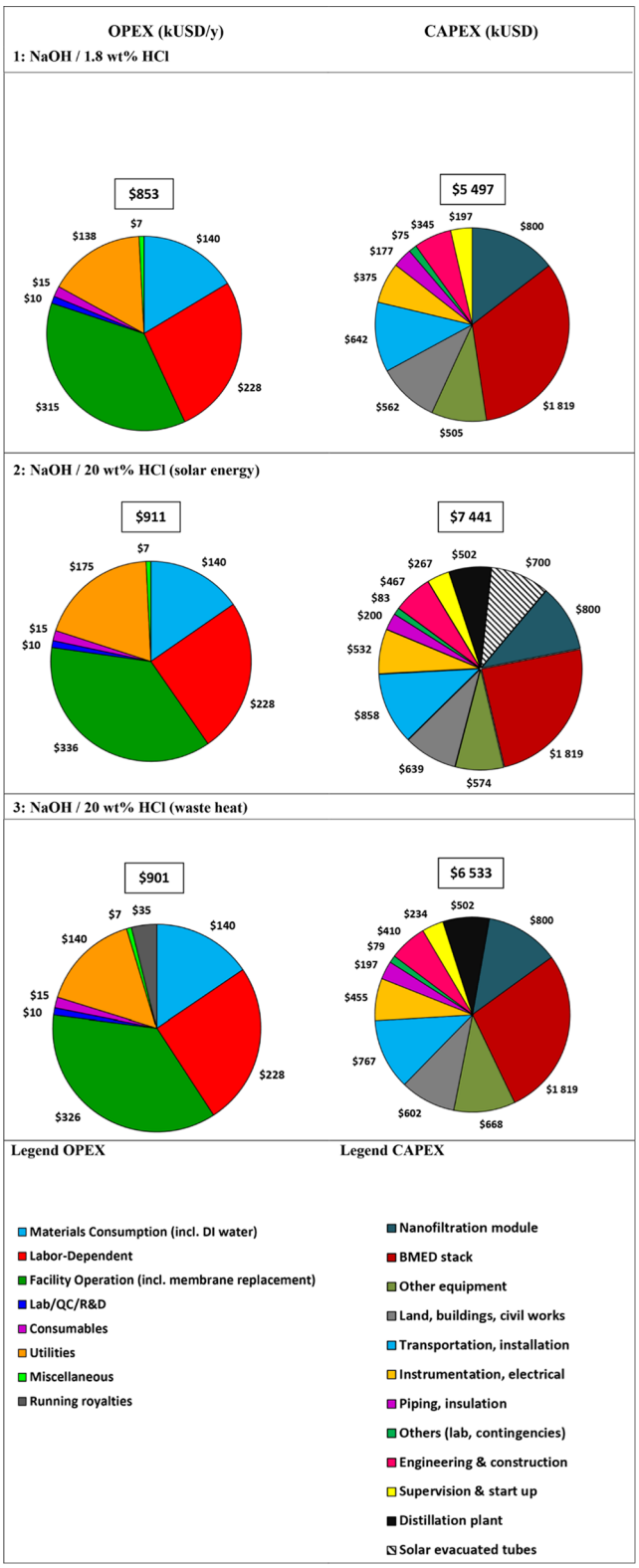


Figure 2. Total cost for each scenario divided into OPEX (thousand USD/year) and CAPEX (thousand USD) in which a BMED system, fed with nanofiltration-treated desalination brine, is used to produce 2.1 wt % NaOH and HCl at various concentrations according to three scenarios: Scenario 1, 1.8 wt % HCl produced with no distillation; Scenario 2, 20 wt % HCl distilled using solar energy; Scenario 3, 20 wt % HCl distilled using waste energy from a nearby natural gas plant. In all scenarios NaOH is produced at 2.1 wt %).

OPEX calculations: Figure 2a shows the share of each operating cost. Facility-dependent costs (e.g., membrane replacement every three years, maintenance and repairs, insurance and local taxes) and labor represent the highest annual costs, followed by raw materials and electric energy. The greatest operating cost associated with facility-dependent costs is due to membrane replacement. The minimum personnel to operate the plant is one plant manager and three specialized workers, who each work 8 h/day. The labor gross cost accounts for 228 000 USD/year.

Raw material cost is primarily for deionized water, which is needed at the beginning of every stack cycle in the HCl and NaOH tanks. Its quantity, 92 400 m^3/year, and its cost (138 600 USD/year) are non-negligible and account for 99% of the raw materials and 16.2% of the total technical annual operating costs. A few reagents are needed at plant start-up to increase the conductivity of deionized water in the anodic and cathodic side. Sodium sulfate is added to the electrode rinse solution of the BMED stack, but is not consumed, and only a small makeup volume will be needed from time to time to maintain its total volume.

The electric energy cost is nearly 138 000 USD/year with a substation power of 493 kW. The cost of the electricity was set at 0.061 USD/kWh with the hypothesis that all the energy is fully renewable and produced from wind turbines. The breakdown of the electrical consumption is listed in Supporting Information.

Loan payments were calculated considering an annual compound interest for a repayment period of 10 years. In general, the more frequently loan payments are made, the lower total interest that must be paid.

We used the revenue stream for the plant, i.e., dilute HCl, to determine the levelized cost of CO_2 removal. The dilute (1.8 wt %) HCl solution may be sold at 9 USD/t, which was linearly extrapolated from the cost of 20 wt % HCl and considering that approximately 46 600 t/year are produced, this byproduct accounts for 420 000 USD/year, making it the primary revenue stream. Detailed calculations of the DFC can be found in the Supporting Information. The Economic Evaluation Report (EER) is summarized in Table 2.

Table 2. Economic Evaluation Items and Levelized Cost of CO_2 Captured (Scenario 1, 1.8 wt % HCl Produced with No Distillation; Scenario 2, 20 wt % HCl Distillated Using Solar Energy; Scenario 3, 20 wt % HCl Distilled Using Waste Energy from a Nearby Natural Gas Plant[a]

Scenario	1	2	3
Equipment purchase cost (million USD)	3.124	4.396	3.789
Direct fixed capital (million USD)	5.497	7.441	6.533
Working capital (million USD)	0.513	0.550	0.515
Total capital investment (million USD)	6.045	8.026	7.082
Revenues (million USD/year)	0.486	0.466	0.466
Total OPEX (million USD/year)	1.363	1.554	1.483
Levelized cost of CO_2 removal (USD/t)	848	1076	998

[a]In all scenarios NaOH is produced at 2.1 wt %). All three scenarios have the same start-up costs (20 000 USD), up-front R&D (15 000 USD) and the same total amount of CO_2 captured (878 tons of CO_2/year).

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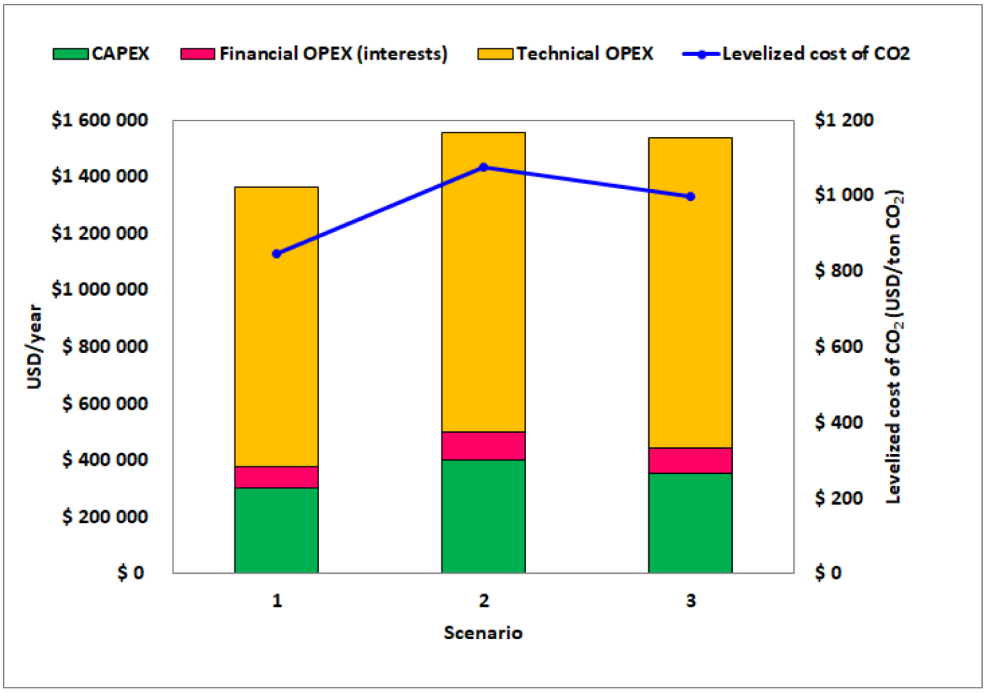


Figure 3. Share of CAPEX, financial OPEX (interests on the capital expenditures), and technical OPEX in the three scenarios (Scenario 1, 1.8 wt % HCl produced with no distillation; Scenario 2, 20 wt % HCl distilled using solar energy; Scenario 3, 20 wt % HCl distilled using waste energy from a nearby natural gas plant. In all scenarios NaOH is produced at 2.1 wt %). Revenue from the sale of HCl is deducted from the total expenditure to provide a levelized cost of 1 ton of CO_2.

Profitability is not achieved because the gross profit is negative (revenues < total OPEX). The main cost drivers include loan payment at current interest rates, the facility-dependent, raw materials, labor, and energy costs. Since OPEX is greater than the plant's revenues, we did not assess the impact of the time value of money. To make a profit, therefore, the removed CO_2 must be valued as a credit. A carbon credit price of 848 USD/ton of CO_2 would achieve a breakeven point for this scenario (no discounted cashflow (DCF) considered). Considering three different values for opportunity cost of capital (2%, 5% and 7%), the breakeven point is 905, 964, and 1002 USD/ton, respectively. This value was calculated matching the averaged total OPEX (i.e., those including technical and financial operating costs) with the averaged revenues, both annually increased at a 1.5% inflation rate. It should be noted that this reasonable carbon credit assumes the improbable scenario that there will be many large industrial consumers of dilute 1.8 wt % HCl. The remaining scenarios assume more realistic outcomes.

4.2. Distillation of HCl to 20 wt % Commercial Grade.

In Scenario 1, it was assumed that the direct sale of 1.8 wt % HCl solution was possible, but the reality is that there are few, if any, buyers of such dilute HCl. An alternative is thus to upgrade this byproduct to commercial grade. HCl is usually sold at 37 wt % (fuming acid). However, achieving this high concentration requires extractive distillation or a dual-pressure technology to overcome an azeotrope at a concentration of 20.2 wt % that occurs at 106.9 °C and atmospheric pressure. The higher CAPEX involved was calculated to be greater than the increase in revenue (details discussed in Supporting Information). For this reason, a concentration of 20 wt % was considered sufficient for its valorization, avoiding extractive distillation with sulfuric acid or calcium chloride and with sufficiently high concentration to be realistically salable. Scenario 2 thus includes the EPC for a small distillation plant (capacity 6 m^3/h), one chiller and enough solar evacuated tubes to power the system, detailed in the Supporting Information. The number of tubes was calculated according to the total thermal energy required for distillation and the unit production of tubes commercially available. Some electric heaters, powered by green energy (e.g., wind turbines) are provided as support when the solar radiation is insufficient, for instance during the night or on cloudy days. Solar evacuated tubes and electric heaters were used for the distillation to avoid CO_2 emissions from conventional thermal fossil fuel powered distillation. In simulations using thermal distillation, the overall process was a net CO_2 emitter, negating the purpose of the BMED system. If the plant combusted methane to achieve the needed thermal energy, the consumption would have been 418 N m^3/h with an associated cost of nearly 163 000 USD/year. Furthermore, approximately 6522 tCO_2/year would be emitted, which far exceeds the 878 tons of CO_2/year removed. This would only have offset an estimated 2900 tCO_2/year (calculations presented in the Supporting Information) emitted from the conventional production of HCl, invalidating the purpose of this OAE plant. Solar concentrators allow the column bottom temperature to achieve 106 °C, however the capital investment is approximately four times higher than that of a gas boiler. Technical OPEX are shown in Figure 2.

Revenues for this scenario are based on the sale of 20 wt % HCl solution, whose price is estimated at 100 USD/t. The total revenue is nearly 403 000 USD/year. Electric energy consumption is greater than the previous scenario because of the additional equipment to distill the dilute acid; the electrical energy costs 175 000 USD/year. Further, the total installed power is higher at 570 kW as compared to 493 kW. The other assumptions including repayment period, interest rate,

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electricity price, etc., remain unchanged, (details presented in Supporting Information). The EER is summarized in Table 2.

The profitability analysis is worse than that of the previous scenario. This is due to lower revenue from the sale of HCl (the unit cost is higher, but the quantity is lower), greater electric consumption and, above all, a considerable annual loan that increased because of the cost of the solar tubes. As such, a carbon credit price of 1076 USD/ton of CO_2 would be required to achieve a breakeven point for this scenario (no DCF). Considering an opportunity cost of capital of 2%, 5% and 7%, the breakeven point is 1125, 1204, and 1254 USD/ton, respectively.

4.3. Distillation of HCl to 20 wt % Solution Using Waste Energy. Scenario 2 produced a salable 20 wt % HCl but was significantly less economical because of the cost of solar evacuated tubes needed to operate the distillation column without CO_2 emissions. Scenario 3 is similar to Scenario 1, i.e., it envisages the sale of 20 wt % HCl solution, but the thermal and cooling energy used in the distillation column are supplied as waste heat and spent or excess cooling water from a neighboring power plant. This case implies another constraint, aside from colocation with a desalination plant: the OAE facility must be built in proximity to a power plant with availability of waste heat and cooling water. In our assumption, such a plant is fueled by natural gas with a gas-turbine cycle, without recovery of heat from flue gas. Furthermore, the OAE plant can take advantage of the cooling water used there. This favorable situation occurs in several places around the world, and exists in our model location of Carlsbad city, CA.

The EPC always includes the distillation column and its auxiliaries including a reboiler, condenser, upstream heat exchanger, and pumps, in addition to the cost of valves and piping to connect the two facilities (150 000 USD). This scenario is environmentally friendly as it uses waste energy from another existing facility, achieving industrial symbiosis. The total installed power is 497 kW which is lower than Scenario 2 (570 kW) and similar to Scenario 1 (493 kW). Figure 2 shows the share of each technical operating cost. Such OPEX includes an additional item, that is a running royalty (35 000 USD/year) provided to the power plant for the transfer of thermal energy and cooling water. The EER is summarized in Table 2.

Despite the use of nearly free thermal energy and cooling water, Scenario 3 also fails to achieve a positive gross profit based solely on the sale of 20 wt % HCl solution. As such, a carbon credit price of 998 USD/ton of CO_2 would be required to achieve a breakeven point (no DCF). With an opportunity cost of capital of 2%, 5% and 7%, the breakeven point is 1049, 1119, and 1163 USD/ton, respectively.

5. COMPARISON OF THE DIFFERENT SCENARIOS

The comparison among different economic parameters is reported in Figure 3 and Table 2. The scenario that provides a direct sale of diluted acid is undoubtedly the most economically viable, despite requiring carbon credit sales for profitability.

The technical operating costs consider all annual expenses excluding financial ones, i.e., the loan repayment. They are shown in Figure 2.

CAPEX is greatest in Scenario 2 (distillation with solar tubes, 20 wt % HCl) due to the investment in solar evacuated tubes, while in Scenario 3 (distillation with waste heat, 20 wt % HCl) there are additional costs associated with the connection of the OAE plant to the power plant for supplying steam and cooling water. The interest payments change proportionally. The cost of the BMED stack is mainly due to membranes, and accounts for 67% of the 1.8 million USD required to purchase the electrochemical apparatus.

The most significant technical OPEX in all three scenarios is related to facility-dependent costs, which above all is due to the replacement of membranes as well as maintenance and repairs, insurance and local taxes. Since the lifetime of the membranes is estimated to be three years, six replacements are required throughout the project lifespan, the total cost of which, spread over 20 years, is nearly 256 000 USD/y. This represents >75% of the total facility-dependent costs and >25% of the total OPEX for the plant. This is the first cost that researchers should aim to reduce, by developing more scalable, more efficient, and longer-lasting membranes with lower production costs. This will reduce their purchase cost, the number of replacements, and increase their efficiency with a lower stack energy consumption. Moreover, improved membranes may withstand higher ion concentrations (Ca, Mg), reducing or eliminating the need for NF pretreatment, which would further save both CAPEX and OPEX.

OPEX is lowest in Scenario 1 (no distillation, 1.8 wt % HCl). The most significant difference between Scenario 1 and Scenario 2 and 3 is that the electrical consumption and utility costs are higher when distilling HCl, which requires more pumps for fluid circulation in the column (Scenario 2 and 3) and uses solar tubes and chillers (Scenario 2).

Figure 3 shows the share of the overall OPEX, split into annual technical OPEX, CAPEX payments averaged over 20 years, and annual financial OPEX, i.e., interest payments on the total CAPEX. To uniformly compare the three items annually across all three scenarios, CAPEX and interests were spread over 20 years, i.e., the project lifetime, even though they are paid back in ten years.

Table 2 lists the main items composing the total investment, i.e., CAPEX, total OPEX (sum of technical and financial) and the levelized cost required to remove one metric ton of CO_2: this value was calculated by subtracting the weighted unit revenue per ton of CO_2 from each item composing the annual costs per ton of CO_2, e.g., CAPEX, raw material, labor, facility-dependent, R&D, consumables, and utilities, and thus summing the resulting partial values.

Hence, the levelized cost of CO_2 (LCO_2) considers the sale of the byproduct, namely the HCl solution, that is necessary to reduce the carbon credit cost.

In terms of economic performance and the LCO_2, the best scenario is Scenario 1. The LCO_2 values for each scenario are as follows: Scenario 1: 848 USD/ton, Scenario 2: 1076 USD/ton, and Scenario 3: 998 USD/ton. The main challenge in Scenario 1 is the low concentration, and hence large volume, of the HCl byproduct, which makes it impractical to transport and sell. As a result, the only feasible option is to use the dilute HCl onsite for manufacturing chlorine products, but this too is impractical for various reasons including that it adds plant complexity, increases logistical difficulties, and requires market alignment. The LCO_2 in both Scenarios 2 and 3 increases by 27% and 17%, respectively, compared to Scenario 1, but produces a higher concentration of HCl that could be sold. These scenarios could generate higher revenues compared to Scenario 1, however, the increase in OPEX is greater still (caused by increased energy consumption) making these scenarios more expensive. This detailed quantification

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indicates that addressing the use of HCl will have a > 20% impact on the LCO_2 and improve the overall economics of the process.

Table 3 shows the electrical consumption per kg of NaOH and HCl generated, considering the total annual electrical consumption. These values are also divided into plant sections, i.e., upstream of the BMED (NF pretreatment and delivering of deionized water and brine), the BMED-stack (including the four recirculation pumps) and downstream of the BMED, the latter considering discharge of NaOH and spent brine into the ocean and HCl distillation, if used.

Table 3. A Breakdown of the Energy Required per Unit Operation to Operate the OAE Plant to Remove 878 tCO_2/year (Scenarios: 1—No Distillation; 2—20% HCl Solar Energy; 3—20% HCl Waste Energy)[a]

Scenario	1	2	3
As a function of generated 100% NaOH/HCl			
Total electrical consumption (kWh/kg)[b]	2.27/2.74	2.88/3.48	2.30/2.78
Upstream	0.10/0.12	0.10/0.12	0.10/0.12
BMED system	2.09/2.53	2.09/2.53	2.09/2.53
Downstream	0.05/0.06	0.66/0.80	0.08/0.10
Other equipment	0.03/0.03	0.03/0.03	0.03/0.03
Total unit cost[b] (USD/t)	1366/1649	1557/1881	1539/1858
As a function of removed CO_2			
Total electrical consumption (kWh/kg)	2.58	3.27	2.61
CO_2 emitted by HCl transportation (t/year)	400	33	33
Avoided CO_2 emissions replacing conventionally produced HCl (t/year)	2900	2900	2900

[a]Additional CO_2 emitted in operating the plant is listed. [b]Considered as 100% NaOH and HCl.

Most of the total consumption is due to the BMED stack. Furthermore, the electrical unit consumption to produce NaOH and HCl (2.27−2.88 and 2.74−3.48 kWh/kg) are in line with those estimated by other literature studies, at bench-scale and sometimes with synthetic seawater or brine[14,15,17,33,34] and at pilot scale.[18,35,36] The third to last row of Table 3 reports the unit energy consumption per kg of CO_2 removed, assuming that 0.8 mol of CO_2 are removed for every 1 mol of NaOH added to the oceans. The lowest energy consumption is related to Scenario 1 (2.58 kWh/kg) as there is no distillation, whereas the most intensive is Scenario 2, whereby the OAE plant must use heating and cooling utilities (3.27 kWh/kg).

5.1. CO_2 Emissions. Another crucial aspect to consider when evaluating the performance of OAE technology is its environmental sustainability, i.e., the net balance of CO_2 emission. Since it is not always possible to use 100% renewable energy, for instance for transportation of products, it is important to minimize potential CO_2 emissions. There are indirect emissions related to the transportation of the final HCl solutions and emissions associated with distillation.

The second last row of Table 3 lists the CO_2 emissions of the scenarios investigated. The transportation of the commercial grade HCl to the final storage warehouse by diesel-fueled tanker trucks generates indirect emissions. To estimate these emissions, a standard 7000-gallon truck used for chemicals transportation and a plant-client distance of an 80 km round trip were considered. The average unit emission of a diesel truck is 53 gCO_2/ton•km and considering that in half the trips the tanker truck is full and in half it is empty, we calculated the emissions from all required transportation. The detailed calculations for HCl transportation are presented in Supporting Information.

Importantly, the least expensive option (Scenario 1) also generates a large amount of CO_2 (400 t/year) from the transportation of large volumes of dilute HCl (1.8 wt %) assuming diesel trucks. As such, the effective amount of CO_2 removed is only approximately half of the target (478 t/year vs 878 t/year), which makes the *effective* levelized cost of CO_2 for Scenario 1 nearly twice the calculated value.

Scenario 2 requires HCl distillation, with direct CO_2 emission: if thermal energy was generated by combustion of methane of natural gas, the CO_2 released into the atmosphere would be 6522 t/year, e.g., the plant would emit roughly seven times more CO_2 than that removed. For this reason, we have chosen to use evacuated tube solar collectors, which are able to achieve the temperature required to concentrate HCl; the system is reliable and considering the solar radiation seasonally available in south California it is possible to supply the required thermal energy designing the number of tubes. The successful integration of BMED with renewable energy sources such as solar photovoltaic (PV) has previously been investigated by Herrero Gonzales et al.[37] Nevertheless, this is the first time that thermal solar energy has been assessed to distill HCl.

Finally, the HCl produced from BMED and sold would displace HCl on the market synthesized through the conventional chloralkali process. The estimated carbon footprint of HCl production (0.89−1.20 kg CO_2/kg 30 wt % HCl) is associated with approximately 2900 tons of avoided CO_2 emissions (calculations presented in the Supporting Information), listed in the final row of Table 3.[38,39] These avoided emissions would not qualify for carbon credits but contribute to the total CO_2 emissions removed and/or avoided by this process.

6. REQUIREMENTS FOR OAE PLANT PROFITABILITY

In all the scenarios we focused on the calculation of the levelized cost of CO_2 considering the sale of HCl as the sole revenue of the OAE plant. Since all the three scenarios showed a negative overall economic balance, it was useful to find which carbon credit price corresponds to the breakeven point of the OAE plant. The breakeven point depends on the valorization process of the HCl solution. This calculation was discussed above for the three scenarios, and was 848, 1076, and 998 USD/ton of CO_2, for Scenarios 1, 2, and 3, respectively.

We further investigated what the carbon credit value would need to be to have a minimally profitable OAE plant. The cost of the carbon credit was selected to have a PI constant at 1.03, while also checking the other indexes that must be simultaneously satisfactory. The PI indicates that for every dollar invested, the OAE project generates 1.03 discounted USD after 20 years.

The most significant indexes from the discounted cash flow analysis are summarized in Table 4 for three different opportunity cost of capital values.

Scenario 1 offers the lowest carbon credit value for an opportunity cost of capital equal to 2%, i.e., compared to a low-risk alternative investment.

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Table 4. Results of the Discounted Cash Flow Analysis Achieving a Profitability Index (PI) of 1.03, for Different Scenarios to Remove 878 tCO_2/Year[a]

Scenario	1	2	3
Opportunity cost of capital	2%		
Carbon credit value (USD/tCO_2)	1395	1770	1620
NPV (million USD)	6.23	8.27	7.30
IRR (%)	32	32	32
DPBT (years)	5−6	5−6	5−6
Opportunity cost of capital	5%		
Carbon credit value (USD/tCO_2)	1630	2085	1900
NPV (million USD)	6.23	8.27	7.30
IRR (%)	48	49	48
DPBT (years)	3−4	3−4	3−4
Opportunity cost of capital (%)	7%		
Carbon credit value (USD/tCO_2)	1805	2315	2100
NPV (million USD)	6.23	8.27	7.30
IRR (%)	62	62	62
DPBT (years)	2−3	2−3	2−3

[a]Scenario 1, No distillation; Scenario 2, 20% HCl produced by distillation using solar energy; Scenario 3, 20% HCl produced by distillation using waste heat.

The investment is recovered in less than 6 years, i.e., when the annual DCF becomes positive in cumulative cash flow (see Excel files in Supporting Information): that is the DPBT. The cost of the carbon credit can be lowered to provide good economic indices, but the DPBT is too long, i.e., the investor time-horizon is too long for them to recover their investment.

The IRR is a profitability measurement with respect to the opportunity cost of capital: hence, this project would be highly profitable with the calculated carbon credits presented in Table 4 and would be preferred to financial products such as stocks or bonds that have a profitability rate of 2% or less.

The worst scenario is Scenario 2 (dilute HCl distilled to 20% using carbon-free energy produced on site), whereby the greatest CAPEX and OPEX require a minimum carbon credit price of 1770 and up to 2315 USD/credit, this latter high carbon price assumes the opportunity cost of capital is as high as 7%.

Scenario 3 with energy provided by the power plant is an intermediate case, and the OAE investment becomes attractive if the unit carbon credit price is at least 1620 USD for an opportunity cost of capital of 2%. While these costs of carbon credits seem high with respect to what is reported in the academic literature, they are in line with average current prices in the voluntary carbon market (VCM).

7. DISCUSSION

Use of brine as feedstock increases the overall conversion yield to NaOH, keeping constant the other process parameters, but the closed loop plant is not profitable, regardless: this implies that using seawater instead of brine will lead to a worse economic outcome considering that it must be pretreated with chemicals (e.g., antiscalant, biocides) and treated with NF to remove divalent ions before being sent to the BMED process, and is less ionically conductive than brine.

Some studies have demonstrated greater energy efficiency than our results, for instance with higher NaOH and HCl final concentration,[19,33] shorter electrodialysis time[19,36] or lower energy consumption,[19,33] but the profitability even with these more optimiztic values would not improve substantially. Moreover, in some extreme working conditions the membranes run the risk of being damaged or their lifespan severely shortened.

Attention should be paid when comparing unit consumption and costs of BMED processes, as groups obtain such data in very different conditions. For instance, variations between research groups include process time, using synthetic or real seawater and brine, volumes, flow rates, number of triplets, type of membranes, configuration, current density, voltage. As such, the ranges of SEC recorded by researchers is broad ranging from 1.3 kWh/kg of HCl to 9 kWh/kg of HCl, with our value on the lower range (2.74−3.48 kWh/kg of HCl).[33] For instance, Ruan et al.[19] used a real brine as feedstock in a lab-scale BMED stack; they obtained a maximum concentration of acid and base of 1.88 and 2.01 mol/L, respectively, with a current efficiency (CE) of 64.7%, an energy consumption of 3.97 kWh/kg NaOH, and a calculated cost of NaOH at 1.73 USD/kg. Compared to our most expensive Scenario 2 (20 wt % HCl with solar thermal energy), both their unit consumption and cost are higher than our worst-case scenario (2.88 kWh/kg NaOH and 1.56 USD/kg NaOH). Experimental trials conducted with high current (up to 10 A) can achieve high NaOH concentrations in shorter timeframes; however, this will limit the lifetime of the membranes and lead to high unit energy consumption.

One research group that works with one of the largest scale BMED systems (19.2 m^2 membrane surface area) in a small pilot plant in Sicily, obtained their best results operating at 200 A/m^2, in closed-loop (batch) configuration, with a specific energy consumption (SEC) of 1.4 kWh/kg of NaOH and a CE of 80%.[18]

In contrast, when they operated their system in the feed and bleed (F&B) configuration, with a current density of 200−500 A/m^2, the SEC was in the range of 3−3.6 and 1.8−2.7 kWh/kg for acid and base. The highest concentration of acid and base was 0.84 and 1 mol/L, respectively.[36] The same group

Table 5. Summary of Some of the Most Recent Results Obtained in NaOH and HCl Production from Seawater and Brine Using BMED in OAE

Feed	NaOH conc. (M)	HCl conc. (M)	NaOH (kWh/kg)	HCl (kWh/kg)	CO_2 (kWh/kg)	Current efficiency, CE (%)	Cost USD/tCO_2	Reference
NaCl 0.8M	0.53	0.50	2.8−3.8[a]	-	3.2−4.3	82	373−1076	15
NaCl 1 M	3.6	3.3	22.6	43.5	25.7[a]	-	-	33
NaCl 1 M	3.6	3.3	21.2	-	24.1[a]	-	-	41
NaCl 1 M	0.1	0.1	1.16−1.73	-	1.3−2.0[a]	99.4	-	42
NaCl 1.3 M	0.54	0.49	2.0	2.5	2.58−3.27	70−80	848−1076	This work

[a]Calculated values assuming 0.8 mol of CO_2 captured per 1 mol NaOH added to the oceans.

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obtained different results in a closed loop configuration with a brine-fueled stack equipped with five triplets and a membrane surface of 100 cm^2. The final concentration and SEC were approximately 0.48 and 0.45 mol/L, 1.78 kWh/kg and 2.19 kWh/kg on average for base and acid.[35]

In addition to varying conditions, the economic analyses in other papers do not consider all the expenses required to operate a real chemical plant, as we have done in this work, along with updated 2024 costs. The scale of the analysis is also crucial, especially when considering the costs of the BMED stack, which is the most expensive device in the plant, and for which there are no published reference cases with costs. To estimate this critical component, Zaffora et al.[40] calculated the sum of membranes and stack costs and estimated peripherals as 50% of the stack's cost: this value agrees with our estimation.

Table 5 lists the most recent papers that evaluated the consumption and cost of the BMED processes. Each group operated the electrodialysis in very different conditions and thus it is rather difficult to compare the results. Nonetheless, it is helpful to note that Herrero-Gonzales et al.[33] reported HCl and NaOH concentrations up to 3.3 and 3.6 mol/L, respectively, 50% higher than any other found in the literature. Despite that, the SEC of the BMED stack was very high, and the durability of the membranes will likely be very short. The high concentration of NaOH and HCl that was produced in their work, while favorable, is reflected in the exceedingly high energy consumption. The same group demonstrated that the levelized cost of NaOH using PV was reduced by 20% compared to the electrical grid mix, achieving 0.25 USD/kg of NaOH: therefore, the reduction of electricity cost offsets the higher investment in PV panels.[37]

Using secondhand units or minimizing construction costs can slightly increase profitability, but this investment remains far from being attractive to investors. As such, the valorization of the byproduct HCl is crucial for OAE plant profitability. Efforts must be directed into valorizing this stream, and in so doing processes requiring high heat should be largely avoided due to the additional CO_2 emissions.

Considering our process, the cost of carbon credits required to have a minimum acceptable profitability that makes OAE plants attractive, i.e., comparable to that of alternative investments, should be at least 1395 USD/tCO_2 in the case of sale of diluted HCl solution.

As shown by our study, most of the plants based on BMED or direct electrosynthesis (DE)[17] are not profitable. Hence, other types of financial incentives are necessary, for instance investment credits spread annually that can be subtracted from the overall purchase cost or the yearly loan repayment.

8. FUTURE OUTLOOK FOR OAE

Despite the high investment and operating costs calculated herein required to run a full-scale OAE plant to produce dilute HCl as a byproduct, there is significant potential for future cost reduction and optimization, especially considering renewable energy use. This increases the prospective economic viability of OAE technology at full scale.

8.1. Key Drivers of Future Cost Reduction. There are five primary cost drivers for the current electrochemical OAE system, whose costs will undoubtedly decline in the future: (1) membrane cost, (2) membrane lifetime, (3) membrane efficiency, (4) energy cost, and (5) NF module cost.

The bipolar and anion exchange membranes need to be improved in three key ways: (1) cost, (2) lifetime, (3) separation efficiency. Lower costs will occur in part as demand increases leading to economies of scale, but significant immediate cost reduction can be achieved by developing scalable roll-to-roll processing methods, like those used in industrial RO membrane manufacturing. Recent work by several research groups shows promise in reducing both materials and processing costs.[43−45] Increasing membrane lifetimes will limit the number of membrane replacements needed over the plants' lifetime. This can be achieved using polymers that are more resistant to chlorine attack, incorporating monomers into the polymers protect from reduction, or protecting the polyamide layers of the anion exchange and bipolar membranes through coatings and surface functionalization; strategies that have been extensively researched for RO membranes.[46] More robust materials will also allow for the use of antiscalants, which can prolong membrane lifetime and allow membranes to be used with higher concentration feeds.[47] Finally, the separation efficiency can be improved by increasing the selectivity of the membranes toward the ions of interest (Cl^- for AEMs, Na^+ for CEMs). Selectivity is a function of the type and density of the fixed charge groups within the polymers. Recent research has pointed toward trade-offs that exist between selectivity and permeability, which should be used as a guide for experimental materials improvements.[48−50]

We estimated a full membrane stack replacement every 3 years, leading to 6 replacements over the 20-year lifetime of the plant, which aligns with current estimates in the literature and our preliminary experimental assessment. Assuming the above suggested improvements, within ten years we might estimate a membrane lifetime of 5 years, leading to 3 replacements over the plant lifetime and a subsequent cost reduction of 50%. We have not estimated the reduction in costs of the membrane themselves as this is highly dependent on the scale on which this technology is adopted and the development of roll-to-roll processes for these membranes, which has not been demonstrated in the literature yet and is still many years away from industrial implementation.

Moreover, the cost of renewable energies is expected to continue to decrease because of increasing capacity from installed plants worldwide. In some regions of the world, a negative cost of electricity during certain times of the day is likely because of overproduction (e.g., low overnight consumption and overproduction from wind and nuclear power). Negative energy costs have already occurred in some regions when production exceeds demand. Thus, it is reasonable to predict a reduction of 25% in electricity prices.

Another possible improvement is eliminating the NF pretreatment stage, which would reduce the CAPEX by 18−26% and the associated annual energy costs by 2−3%. This may be possible if new membranes (BMP, AEM, CEMs) are made more resistant to magnesium and calcium scaling or are able to be treated with aggressive antiscalant chemical treatments, as proposed above.

While current interests' rates on borrowed capital are higher than in the past 20 years, these rates will likely decrease. A stable 10-year rate of 2.75% is a reasonable hypothesis, further enhancing the financial viability of CO_2 capture projects.

As this paper has shown, the valorization of HCl as a byproduct presents significant challenges due to the high cost of concentrating such a solution to a marketable grade.

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Further, huge volumes of byproduct are expected considering scale-up to capturing gigatons of CO_2. Therefore, it is crucial to identify other viable byproducts, with higher added value, that will not saturate a single market, which are easy to transport and commercialize. This may require the production of different byproducts for different locations and different economies, necessitating new BMED feeds or configurations. These alternative byproducts are the intense focus of ours and other research groups around the world.

8.2. Projected Cost Reductions for CO_2 Removal. The simulations were thus repeated under the cost reduction hypotheses above to provide an outlook on the likely future cost of this technology. The parameters that were changed are

- electricity cost: 0.045 USD/kWh
- capital interest rate: 2.75%
- no NF pretreatment
- membrane cost reduced by 50% (3 replacements, each after 5 years)
- reduction of the stack electric consumption by 25%

The results showed that the levelized cost of CO_2 removal decreased significantly in each of the three scenarios; these values resulted in 394 USD/t CO_2 (no distillation), 601 USD/t CO_2 (20% HCl solar energy), and 539 USD/t CO_2 (20% HCl waste energy), respectively. This translates to a reduction of more than 50% of the levelized cost of CO_2.

Another aspect that was not considered but that will contribute to lower overall CO_2 levelized costs is the plant's capacity. If the aim is to remove at least 1 Gton of CO_2 annually by this technology by 2050,[41,42] and we hypothesize at least 100 plants built and operating worldwide, each one should be sized to remove 10 million tons of CO_2 each year. It is well-known that CAPEX is not linearly proportional to the capacity, and thus, the total CO_2 levelized cost is expected to decrease further. Our analysis did not consider any governmental financial support in purchasing equipment and devices (investment tax credit) or tax credits, e.g., tied to operation, providing owners with production tax credits per ton of carbon captured by the plant over its life span. These additional financial measures will boost the investment in CO_2 capture projects and enhance their feasibility.

8.3. Comparison in the Current Market. When we compare the three levelized costs determined using the above assumptions, we find that they align with the range indicated by some reports for the OAE method based on electrochemical approaches (reported as >500 USD/tCO_2).[51] In comparison, costs in the range of 100−150 USD/tCO_2 that have been estimated in the literature for OAE plants with mineralization techniques,[51] seem unrealistic based on our more complete analysis. Our results in Tables 2 and 4 demonstrated that the production costs are high, and that profitability can only be achieved by selling carbon credits at prices far greater than 1000 USD/tCO_2. Considering the carbon credit prices of emission trading systems (ETS) in many countries (in the range of 50−120 USD/t CO_2), OAE would seem to be vastly too expensive. However, the potential of OAE is still promising when compared to carbon prices on the voluntary carbon market (VCM), which gives companies, governments, non-profit organizations, and individuals the opportunity to buy and sell carbon offset credits. Of note, some platforms like Frontier, have recently managed 4.5 million USD of carbon removal prepurchases from several companies (Alithic, Alt Carbon, Anvil, Capture 6, Exterra Carbon Solutions, Flux, NULIFE, Planeteers, and Silica) on behalf of buyers (Alphabet, H&M Group, Stripe, Shopify, and McKinsey) with purchasing prices varying between 270 and 1960 USD/tCO_2, depending on the producer and technology.[52]

The most used technologies currently are DAC, OAE, mineralization, and field weathering. For example, Planeteers, a German start-up company that generates carbon credits via OAE technology, has signed a contract with Shopify Inc. (Canada) and Stripe Inc. (USA), for them to buy the 225 tons of CO_2 carbon credits over three years (2026−2028) for 1960 USD/tCO_2.[52] This confirms that our analysis is aligned with current techno-economic realities and prices, and supports our more representative calculations. By focusing on process improvements listed above (process control, optimization of the storage volumes and spare devices) the levelized cost of CO_2 can be reduced to below 400 USD/tCO_2 even without improved valorization of the HCl.

9. CONCLUSIONS

In this paper, the feasibility of a full-scale BMED plant was studied. The productivity is 140 m^3/day of 2.1 wt % NaOH solution, and the same volume of a 1.8 wt % HCl solution byproduct. The location of the plant was chosen to be in southern California for colocation with a desalination and thermal electricity generating station. A detailed techno-economic analysis was carried out in three different scenarios: direct sale of 1.8 wt % HCl and distillation of HCl at 20 wt % using carbon emission-free thermal energy or waste heat from a nearby thermal electric power plant. The modeled OAE facility achieves a total removal of 878 tCO_2/year on average. The levelized cost to remove CO_2 from the atmosphere was determined to be in the range 848−1076 USD/ton of CO_2, depending on the destination of the HCl solution byproduct.

This price of carbon is necessary to offset the costs of the plant after the sale of the HCl solution byproduct is considered. To achieve acceptable profitability for investors seeking modest returns, however, we estimate that carbon credits would need to be sold for 1395 to 1805 USD/ton of CO_2 in its current iteration. This value is already aligned with some of the current price of carbon credits on the voluntary carbon credit market.

OAE by BMED using desalination brine to split NaCl into NaOH and HCl is not economically feasible in its current state because of the low market value of carbon credits, the high cost of membranes used in BMED, the high electricity consumption in the BMED process, as well as the high costs to distill the byproduct HCl. The results show that the OAE unit cost for removal of CO_2 is still high, and those found in the literature are often underestimated, and frequently lack transparency regarding the included component costs. Moreover, our findings highlight that the byproduct (in this case HCl solution) necessitates proper valorization to realistically offset total costs.

Despite that, BMED remains the most attractive approach for OAE for many practical reasons, thus we propose several directions to lower the levelized cost of CO_2: (1) connect the system to waste electricity from renewable electricity sources, (2) produce salable byproducts other than HCl that can be generated with lower capital and energy costs, and (3) focus on improving the membranes through (a) roll-to-roll scalability, (b) improved chlorine tolerance, and (c) higher selectivity. As such, OAE processes need specific financial support in line with that provided to oil and gas companies to help the

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economies of scale reduce their costs. Though the numbers are still high, the outlook of the OAE technologies is positive as lower interest rates, enhancement of membrane efficiency and durability, coupled with the reduction of electricity cost and consumption can reduce the levelized cost of CO_2 in the range of 394−539 USD/t CO_2.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.4c04364.

Supplemental data, reporting plant description and technical data, equipment purchase cost, CAPEX and OPEX breakdown, electrical consumption for three scenarios (PDF)

Process flow diagram of the plant (PDF)

The calculation sheets of the investigated scenarios (XLSX, XLSX, XLSX)

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Notes

The authors declare no competing financial interest.

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