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Indirect ocean capture of atmospheric CO₂: Part I. Prototype of a negative emissions technology

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ABSTRACT

We present the design, construction, characterization, and analysis of a prototype process for a novel electrochemical platform of candidate negative emissions technologies (NETs), termed indirect ocean capture. The IOC technologies remove carbon dioxide gas from the atmosphere by leveraging both air-ocean gas exchange and the pH sensitivity of the ocean's carbonate buffer system. The system characterized in this paper enables two configurations that capture CO₂ either as a pure gas or as a solid mineral. Both configurations use the acid and base produced by the membrane electrodialysis of ocean water. The first configuration, termed the 'acid process', acidifies ocean water or brine to shift the carbonate buffer system towards dissolved CO_2 gas, which is vacuum stripped from the acidified brine. The second configuration, termed the 'base process', adds base to the brine to shift the carbonate buffer system towards carbonate ions, which precipitates as CaCO₃. A closed loop cycle is achieved by returning this decarbonized and alkalinized brine to the ocean for additional CO₂ absorption from the air. Our evaluation of this prototype scale system focused on the parameters that have the most influence on the ultimate cost of the extracted CO₂. In a concurrent techno-economic study, the most cost-sensitive parameters were shown to be the efficiencies of the anion and cation exchange membranes, the number and orientation of CO2 extraction membranes, and the volume of base required for CaCO3 precipitation. The measured parameters provide target values for commercial deployment. The experiments in this study were used to inform the concurrent techno-economic study that quantifies in detail the projected cost of avoided CO2 achievable with this process.

1. Introduction

Most climate models suggest that limiting warming to 2 °C will require the deployment of negative emissions technologies to start as early as 2020 (Fuss et al., 2016; Rogelj et al., 2016; Rogelj et al., 2015; Smith et al., 2016). This increased concentration of atmospheric CO₂ leads to greater dissolution of CO₂ gas into the oceans, which leads to ocean acidification (Stocker, 2014). Global efforts to reduce CO₂ emissions, for example by phasing out fossil fuel combustion through increased usage of renewable fuels in the energy and transportation sectors, will not address CO₂ already in the atmosphere due to past emissions (Keith, 2009). Remediating past emissions can only be achieved through negative emissions technologies (NETs) (Council,

2015).

Many NETs have been proposed and tested in recent years (Council, 2015; Tavoni and Socolow, 2013). These include ocean liming (Renforth et al., 2013), afforestation and reforestation (Bravo et al., 2017), direct air capture (DAC) of CO_2 (Baciocchi et al., 2006; House et al., 2011; Socolow et al., 2011), bioenergy with carbon capture and storage (BECCS) (Evans et al., 2015; Fajardy and Mac Dowell, 2017; Kemper, 2015; Stavi, 2013; Williamson, 2016), and indirect ocean capture (Mazzotti et al.) (Eisaman et al., 2011a, 2011b, 2012). Ocean liming has the potential to efficiently sequester CO_2 , however there are concerns about the environmental impacts of the required massive land-based mineral extraction, processing, and transportation (Rau, 2014). Afforestation and reforestation negative emissions are limited by

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soil disturbance emissions, slow tree growth, low CO₂ uptake during some stages of tree development, and limited availability of land suitable for tree growth (Evans et al., 2015). Although DAC has significant cost challenges (House et al., 2011; Kriegler et al., 2013; Socolow et al., 2011), commercial projects are underway (Peters, 2015). BECCS is the most mature of the NETs, with commercial plants and mature CO₂ capture technologies available for these plants (US Department of Energy; Venton, 2016). Indirect Ocean Capture (Mazzotti et al.) may be viewed as a hybrid between DAC and ocean liming, leveraging the ocean-atmosphere equilibrium to capture carbon in the ocean, and pH control to extract the CO₂. Until now, IOC remained a benchtop proofof-concept in need of process engineering and techno-economic assessment. The NETs that have been tested to date have opaque and widely varying cost estimates ranging from \$20 to \$1000/tCO₂ (metric ton of CO₂) (House et al., 2011; Jones, 2009; Lackner, 2010; Mazzotti et al., 2013; Pritchard et al., 2015). There is little consensus on the likely avoided CO₂ costs for NETs. Transparent and publicly available cost estimates are needed to properly inform policy decisions regarding the best approaches to combatting climate change (Keith, 2009).

Toward this aim, in this article we describe the construction and assessment of a prototype IOC system based on a previously published lab-scale system. In the article immediately following this one, entitled *Indirect ocean capture of atmospheric CO*₂: *Part II. Understanding the cost of negative emissions* (referred to in this paper as "Part II"), we describe the results of a techno-economic model that inputs the measurements described in this article to calculate the avoided CO₂ cost for IOC (Eisaman et al., 2017).

The IOC process is shown in Fig. 1, which depicts a schematic of the "acid process" leveraging the gas exchange of atmospheric CO_2 with the oceans as a natural mechanism for CO_2 capture and concentration. On a per-carbon basis, the carbon content of the oceans in the form of dissolved inorganic carbon (DIC = sum of dissolved CO_2 gas, bicarbonate (HCO_3^-) ions and carbonate (CO_3^{2-}) ions) is 140 times greater by volume than the carbon in the atmosphere in the form of gaseous carbon (Butler, 1982). In the acid process, we remove DIC from ocean water using a controlled chemical manipulation of the ocean carbonate equilibrium via pH adjustment that uses the acid and base produced by a three-compartment membrane electrodialysis system. IOC has a small physical footprint, can provide high purity CO_2 (99% pure, dry basis), and has a multitude of options for process intensification (co-location

for mutual benefit) with other ocean water-pumping technologies such as desalination, power-plant cooling, and material extraction, for enhanced economics.

In the acid process, a slipstream of treated ocean water is passed through a three-compartment bipolar membrane electrodialysis (BPMED) system (Tanaka, 2007), which produces dilute acid and base from inputs of electricity, brine, and water. This represents an increase in scale and efficiency over the lab-scale experiments, which relied on two-compartment electrodialysis prone to mineral scaling (Eisaman et al., 2011a,b, 2012). The acid generated by BPMED is used to acidify large volumes of filtered ocean water in order to convert all the DIC to CO_2 gas. CO_2 gas is stripped from solution, after which point the base generated by BPMED is used to return the ocean water to its original pH and alkalinity, allowing it to recapture CO₂ from the air after being returned to the ocean. In addition to the IOC acid process, we also developed an alternative implementation that we termed the "base process". The "base process" uses the base produced by BPMED to increase the pH of ocean water to precipitate the DIC as CaCO₃. Upon precipitation of the DIC in the ocean water, CaCO₃ is removed by sedimentation. As in the acid process, this decarbonized and alkalinized ocean water is returned to the ocean surface to continue absorbing CO₂ from the atmosphere.

This study presents the design, experimental characterization, analysis of the closed-loop acid process efficiency, identification of the most cost-sensitive parameters, and recommendations for future optimizations of the IOC prototype system. The data from this study was fed into a techno-economic model described in the *Part II* article (Eisaman et al., 2017) that immediately follows this article. The techno-economic model identifies the most cost-sensitive parameters to be: the effect of anion and cation exchange membrane performance on the system's current efficiency (i.e., Faradaic efficiency), the number and configuration of CO₂ extraction membranes, and the volume of base required for CaCO₃ precipitation. The techno-economic model and the accompanying analysis in the subsequent article (Eisaman et al., 2017) highlight the current cost challenges for IOC and identifies some targeted R&D areas that are most critical to future cost reduction.



Fig. 1. Schematic of indirect ocean capture by pH control of ocean water using the acid process. Zoomin of bipolar membrane electrodialysis (BPMED) shows details of how the BPMED unit is integrated with ocean water for indirect ocean capture.

2. Materials and methods

2.1. Materials

100 ppm TOC Standard Solution and Na₂CO₃ were purchased from Sigma Aldrich. "Instant Ocean Aquarium Sea Salt" (IO) mixture was purchased from Instant Ocean and used to simulate ocean water and brine mineral composition. At 35 parts per thousand (ppt) of IO, the concentration of calcium is 400 mg/L, and of magnesium is 1320 mg/L. Ocean water was made using 0.3 lbs of IO for every 1 Gallon of DI water (35.95 g/L), while brine was made using double this concentration, 0.6 lbs of IO for every 1 Gallon of DI water (71.90 g/L).

A custom built three-compartment bi-polar electrodialysis (ED) stack was constructed by Ameridia, Division of Eurodia Industrie. Membranes from two suppliers were compared to determine optimal ED configuration and operational parameters. ASTOM membranes, supplied by Ameridia, were: Neosepta bipolar membranes (BPM), Neosepta CMB cation exchange membranes (CEM 1), and Neosepta ACM anion exchange membranes (AEM1). Membranes supplied by Asahi-Glass were the Selemion AAV anion exchange membranes (AEM2).

To degas the brine or ocean water before acidification (in the acid process), SuperPhobic membrane contactors purchased from Membrana were used. For CO₂ extraction from acidified brine or seawater Liqui-Cell membrane contactors, also purchased from Membrana, were used. Flow meters, PID controllers, and pH sensors were purchased from Omega. Vacuubrand Mz 2C NT Vario diaphragm pumps were used to separate CO₂ from acidified brine. Condensers to remove water vapor from the CO₂ stream were purchased from LabConco. All basic hardware (valves, tubing, connectors) to construct the prototype system were purchased from McMaster-Carr.

2.2. Methods

2.2.1. Indirect ocean capture (IOC) process

We characterized the performance of two different IOC process flows and quantified the efficiency of their sub-processes. The acid process extracts carbon as CO₂ gas from ocean water by converting DIC to CO₂ gas by making the ocean water more acidic, followed by gas stripping of CO₂; in contrast, the base process extracts carbon as a precipitated solid $CaCO_3$ by converting the DIC to CO_3^{2-} ions by making the ocean water more basic, followed by precipitate settling. In both processes, ocean water or brine is input into the system and dissolved inorganic carbon (Montegut et al.) is extracted from this input solution, either in gaseous or solid form. The most cost-sensitive performance parameters of each sub-process were determined (Eisaman et al., 2017). The sub-process parameters tested were: the efficiency of acid and base production in bipolar membrane electrodialysis (BPMED), the efficiency of membrane contactors in separating CO₂ gas from acidic ocean water, the optimization of acid addition to ocean water to maximally remove carbon as gaseous CO₂, and the optimization of base addition to ocean water to maximally precipitate carbon as solid CaCO₃.

2.2.2. Bipolar membrane electrodialysis

In both the acid and the base process, the first step uses a process known as three-compartment BPMED to produce an acid (HCl) and a base (NaOH) solution.

2.2.2.1. Operation. A BPMED unit was used to produce dilute (1-6 wt %) HCl, dilute (1-6 wt %) NaOH, and H₂O from a stream of brine through the application of a current. As shown in Fig. 2, in a three-compartment configuration a BPM separates the acid from the base and generates hydroxide ions (OH⁻) and protons (H⁺). An AEM separates the acid from the brine and allows the passage of chloride ions (anions, Cl⁻), while preventing the passage of sodium ions (cations, Na⁺) and

 H^+ . A CEM separates the base from the brine and allows the passage of Na⁺, while preventing the passage of Cl⁻ and OH⁻. Each membrane is separated from the other with gaskets, and the entire configuration is sandwiched by positive and negative electrodes, clamped, and sealed. The BPMED stack used for all experiments performed in this study contained seven repeated membrane units.

A process flow diagram of the designed BPMED (Fig. S2) and the detailed procedure for sealing, leak testing, priming, and cleaning the BMPED system are given in the SI.

Upon performance optimization, the ED stack was filled with acid, base, brine, and electrolyte solutions. Each of the solutions was made to flow through the system at a rate of 2.1 L/m (\sim 0.6 GPM). At this flow rate, the maximum pressure applied in any one compartment was 27.6 kPa (4 psi). Ideally no pressure differentials exist between the membrane compartments, but in practical operation pressure differentials can occur due to internal system resistances and small differences in flow rates. The maximum differential pressure that was permitted *between* each of the compartments was 6.9 kPa (1 psi).

2.2.2.2. Current efficiency. Electrical demand was a significant cost to the entire system (Eisaman et al., 2017). The BPMED unit accounted for much of this electrical demand, therefore BPMED current efficiency was carefully measured and optimized.

The current efficiency was calculated by comparing the experimentally determined change in the number of moles of acid or base solution created by electrodialysis, to the theoretical maximum number of moles of acid or base solution that could be formed by the number of electrons (measured in mA) applied to the BPMED stack. As described in Eq. (1), the current efficiency, C_{E-X} , of a solution *X* (where *X* is acid or base), is the ratio of the number of electron equivalent (moles of protons or hydroxide ions) that have crossed the membranes to the number of electron equivalents (moles of electrons) delivered to the entire ED stack through the applied potential. The theoretical maximum number of moles of acid and base is determined by assuming that one mole of electrons delivered by the applied current leads to the formation of one mole of acid and base.

$$C_{E, X} = \frac{\text{effectively transferred electron equivalents}}{\text{theoretically transferred electron equivalents}} = \frac{Q_{experimental, X}}{Q_{theoretical}}$$
(1)

where

$$Q_{\text{theoretical}} = \frac{(n \cdot I \cdot t)}{F}$$

where n is the number of cells in the ED stack, I is the average current applied in Amperes (A), t is the time in seconds (s), and F is the Faraday's constant (96,500 Coulombs/mole of electrons). And where

$$Q_{experimental, acid} = [H^+]_f \cdot V_{acid, f} - [H^+]_i \cdot V_{acid, f}$$

$$Q_{experimental, base} = [OH^{-}]_{f} \cdot V_{base, f} - [OH^{-}]_{i} \cdot V_{base, i}$$

where $[H^+]_i$ and $[OH^-]_i$ are the molar concentration of acid and base obtained *before* applying a current of 10 A for 30 min; $[H^+]_f$ and $[OH^-]_f$ are the molar concentration of acid and base obtained *after* applying a current of 10 A for 30 min; $V_{acid,i}$ and $V_{base,i}$ are the total volumes of the acid and base solutions used in the experiment immediately *before* applying a current of 10 A for 30 min; V_{acid-l} and $V_{base,f}$ are the total volumes of the acid and base solutions used in the experiment immediately *after* applying a current of 10 A for 30 min. The volumes before and after the application of the current vary due to experimental sampling and analysis of the solutions, as well as to electro-osmosis, which draws several molecules of water into the acid and base compartments with each molecule of solute. Measured and calculated current efficiency data were modified to account for the electro-osmotic effect. The details of this calculation and adjustment to collected data are explained in the SI.

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Fig. 2. Three-compartment BPMED schematic. Bipolar membranes (BPM), anion exchange membranes (AEM), and cation exchange membranes (CEM) separate the compartments. Nafion membranes separate the electrolyte and electrodes from the rest of the stack. Percent concentrations represent weight percent (wt.%). Apparent mass imbalances when comparing decreased concentration of brine to increased concentration of acid and base is due to water transport across the membranes.

Electric current data, used to calculate $Q_{theoretical}$, was collected every second and integrated over the length of the experiment. $Q_{experimental,acid}$ and $Q_{experimental,base}$ were determined by measuring the difference between the final and initial acid and base concentrations (in titrated aliquots) over the course of the same timed-experiment. A detailed sample collection procedure is detailed in the SI.

The acid and base current efficiency of two different AEMs was compared. This was achieved by arranging the membranes in two different configurations: 1) BPM-AEM1-CEM1 and 2) BPM-AEM2-CEM1, where AEM1 is Astom ACM membranes and AEM2 is Asahi-Glass AAV membranes. Two different AEM membranes were compared because AEM membranes, made to prevent proton leakage while allowing anions to pass through, have large variability in their efficiency depending on their selectivity and flux. The trade-off between high selectivity (conversely, proton leakage) and high anion flux was expected to have the greatest contribution to BPMED current efficiency. The two selected AEM membranes were optimized for minimal proton leakage within the range of acid concentrations used in these experiments. Each configuration's acid and base current efficiency was evaluated for different acid, base, brine, and electrolyte concentrations. The initial, final, and average acid and base concentrations were determined and calculated by titrations. Table S1 in the SI contains a complete list of all the average solution concentrations that were tested for each membrane configuration. The sensitivity of the membranes to concentration changes was also studied. Extensive experiments on a range of these parameters elucidated the maximum achievable current efficiency



given commercially available materials.

2.2.3. Acid process

Fig. 1 shows a schematic of the BPMED process (2.2.2) coupled to the acid process (2.2.3). Fig. S1 in the SI presents the process flow diagram of the coupled process, and Fig. S2 presents the detailed process flow diagram of the acid process alone, including the flow rates used in the constructed prototype system. pH meters, flow meters, pressure meters, and sample ports are located before and after every input into the brine solution. Solutions of ocean water and brine were made in 1000 L holding tanks. All conditions and membrane configurations were studied for ocean water as well as for brine concentrations. For simplicity ocean water or brine flows will be referred to as brine.

2.2.3.1. Flow path for acid process. Brine is pumped out of the 1000 L holding tank at a flow rate of 10 L/min into three hydrophobic hollow-fiber membrane contactors. Under 30 mbar of vacuum pressure, these membranes degas the input brine by removing dissolved O_2 and N_2 gas. Degassing increases the purity of the CO_2 that is ultimately extracted. Degassed brine is acidified by HCl (2 wt%) produced by the BPMED, which is added to the brine to achieve pH 4. The flow rate (~68 mL/min) is determined by a feedback-controlled peristaltic pump coupled to a pH meter. The added acid converts all the brine DIC in the form of HCO₃⁻ ions and CO₃²⁻ ions into dissolved CO₂ gas. The DIC in surface ocean water is typically around 2 mM, corresponding to an equilibrium

Fig. 3. CO₂ Extraction Membrane Configurations. CO₂ is extracted from acidified brine flowing through hollow fiber membrane contactors in series or in parallel to determine the efficiency of individual membranes.

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partial pressure of CO₂ after acidification of 0.08 atm. Acidified brine is pumped into various configurations of hollow-fiber CO2 extraction membranes contactors, illustrated in Fig. 3. CO2, removed under vacuum pressure across the membrane contactors, is pumped through a cold-trap liquid condenser to remove water vapor. The flow rate of the extracted and dried CO₂ gas is measured with a flow meter at the end of the process train. After CO₂ desorption, NaOH (4 wt%) produced by the BPMED is added to the acidic, decarbonized brine to neutralize the pH and return the alkalinity. The base flow rate is determined by a feedback- controlled peristaltic pump coupled to a pH meter that tracks the brine pH. Adjusting the alkalinity ensures that the parcel of decarbonized brine that is returned to the tank (representing the ocean surface) reabsorbs an amount of CO₂ from the atmosphere equal to the amount of CO₂ extracted in the process. In practice, if one assumes that this water is returned to the surface mixed layer of the ocean (25 m-100 m deep), the time scale for reabsorption of CO2 is estimated to be within one year (Roy-Barman, 2016).

A slipstream of degassed and acidified brine is removed from the process, demineralized, and used in ED as the source of NaCl (aq) to produce HCl and NaOH. This brine volume accounts for less than 1% of the total brine used in the system. Acidified brine is used because the low pH improves the ED current efficiency, while demineralized pure NaCl prevents scale formation (mineral precipitation) in the BPMED system.

2.2.3.2. CO2 extraction membranes. Since we found that the capital costs were very high in large part due to the membrane contactors, we chose to characterize the gas removal properties as a function of flow rate (effectively parallel/series), pressure, DIC concentration, and number in series. The total available DIC for extraction as CO₂ was calculated using the USGS CO2Calc software based on the measured pH, the total alkalinity, and the salinity at STP in the lab. The 'Lueker et al., 2017' model for CO₂ constant as well as the 'Total scale' as the pH scale were used for this calculation. Fig. 3 shows the tested configurations, six membrane orientations, and the naming scheme (1, 2, 3, 1×1 , 2×2 , 3×3) used. In the series configuration, contactors were only connected in series to each other. In the parallel configuration, a second bank of membrane contactors was added in parallel to the first bank. In all configurations, three different vacuum pressures were tested and applied to the permeate side of the membrane contactors for CO₂ extraction: 80 mbar, 55 mbar, and 30 mbar.

2.2.3.3. TC and IC measurements. Total Carbon (Pritchard et al.) and Total Inorganic Carbon (IC) measurements were performed with a GE Sievers InnovOx Laboratory Total Organic Carbon Analyzer (TOC Analyzer). The Total Organic Carbon (Stocker) was calibrated for both standard TOC measurements and TC measurements following rigorous standard procedures that are detailed in the SI. In sum, baselines for TOC and TC/IC measurements were made for all measured solutions including analyzed solutions (brine, ocean water) and flushing solutions (perchlorate, HCl, and DI). The TC was expected to be approximately equal to the IC and expected to vary greatly from < 1 ppm to as high as 100 ppm, since the majority of the carbon in the brine samples was expected to be DIC, and the majority of this DIC was expected to be removed by the acid process. Na₂CO₃ in DI water was used as a TC/IC standard to prepare calibrations (detailed in the SI). Five samples were obtained throughout the experiments: 1) the starting solution (brine or ocean water), 2) a degassed sample, 3) an acidified sample 4) a CO₂-extracted sample, and 5) a NaOH-neutralized sample. TC/IC concentrations were measured in order of increasing expected IC concentration, i.e. in reverse order relative to that used for collection. Two pure DI water samples were positioned before each set of samples to ensure that there was minimal carry-over of IC from one set of samples to the next.

2.2.4. Base process

The base process is similar to the acid process, but with the reverse order of acid and base addition to the brine. The base process can be represented by the schematic in Fig. 1 (showing the acid process) if one exchanges the acid and base arrows for each other. In the base process NaOH is added to the brine in such a way that the pH is maintained near pH 9.3. Precipitation of carbonates can occur at pH > 9, and controlling the pH near 9.3 ensures that solid CaCO₃, and not Mg(OH)₂, is precipitated. Precipitate can be removed through sedimentation, which obviates the need for costly membrane contactors. The base process was evaluated for its feasibility and efficiency, because the techno-economic analysis indicated that the base process is likely a less expensive configuration than the acid process, due to the absence of costly membrane contactors in this design scheme. As in the acid process, both HCl and NaOH are produced in BPMED. Dilute (< 4 wt%) NaOH is added directly to the ocean brine to precipitate out CaCO₃, which reduces the alkalinity. After the precipitation step more NaOH must be added to return the ocean water alkalinity to its original value to enable additional carbon capture from the atmosphere. As in the acid process, a slipstream of the decarbonized brine is used as the source of pure NaCl(aq) for the BPMED.

2.2.4.1. Carbonate precipitation. Two comparative precipitations were carried out – one at high pH in which large volumes of concentrated NaOH were added directly to ocean water, and a second experiment in which small volumes of concentrated NaOH were added in controlled doses to maintain a pH between 9.3 and 9.6.

To maximize the amount of total precipitation $(Mg(OH)_2 \text{ and } CaCO_3)$, a high pH was achieved by adding large volumes of 20.04 g/L NaOH into 3 L of artificial IO ocean water. NaOH was added to the solution step-wise until the pH of the solution increased without the subsequent formation of precipitate.

To maximize the fraction of CaCO₃ (versus Mg(OH)₂) that precipitated out of solution, controlled volumes of NaOH were titrated into ocean water to achieve 9.3 < pH < 9.6. CaCO₃ precipitates optimally in this pH range, while Mg(OH)₂ does not precipitate until pH > 9.6. Basic water with a concentration of 38.26 g/L NaOH was added to the ocean water until a pH of 9.6 was achieved. Precipitate was then allowed to form from solution, spontaneously decreasing the pH as precipitate formed. Once the pH decreased below pH 9.3, more dilute NaOH was titrated into the solution to continue precipitation. This procedure continued until no noticeable drop in pH below pH 9.6 was observed in a 24-h period, at which point it was assumed CaCO₃ precipitation was near complete. Since the concentration of Ca²⁺ is around three times greater in seawater than the DIC concentration ([Ca²⁺] = 10 mM and [DIC] = 3.3 mM, for the 35 ppt IO used to represent seawater in our experiments), no DIC is left at the end of this process.

2.2.4.2. Chemical analysis. In both high and moderate pH precipitation, the solution was separated from the precipitate by decanting the solution from the precipitate. Additional precipitate was extracted from this solution through vacuum membrane filtration. The total separated precipitate was dried at 105 °C for approximately 5 h. Dry precipitate was analyzed by X-ray fluorescence (XRF) and scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM-EDS). A hand-held Thermo-Scientific Niton XL3 t GOLDD + portable X-ray fluorescence (XRF) instrument provided rapid chemical analysis to determine the presence of Mg²⁺ and Ca²⁺, while a Jeol JSM-7400F field emission scanning electron microscope with an INCA x-sight energy dispersive X-ray spectroscopy attachment (SEM-EDS) was used to quantitatively identify the chemical components of the precipitate.

2.2.4.3. Surface analysis. The precipitate was sputtered with Pd/Au and imaged using SEM. The crystal structure of the CaCO₃ precipitate was clearly imaged and compared to the rough, non-crystalline phases of $Mg(OH)_2$.

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Table 1

Energy consumption for individual system components for the acid (left) and base processes, respectively, for the system (CO_2 extraction capacity of 20 kmol(CO_2)/h operating for 341 days per year totalling 7202 metric tons of CO_2 per year) evaluated in the concurrently published techno-economic analysis (Eisaman et al., 2017).

System Component	Best-case, acid system (GWh/yr)	Best-case, base system (GWh/yr)
ED stack	17.9	29.9
Nano booster pump	0.235	0.365
RO booster pump	1.15	1.21
Vacuum pump	2.57	0.108
Vac. pump chiller	0.695	0.011
Additional pumping	Free (driven by RO plant head)	Free (driven by RO plant head)
Pretreatment/filtering Total	Free (done by RO plant) 22.55	Free (done by RO plant) 31.59

3. Results

3.1. System energy and material requirements

The efficiency with which the electrodialysis system produces acid, and the efficiency with which the membrane contactor system extracts CO_2 gas from brine are critical to both the energy and the economic performance of IOC.

The energy requirements for each component of the acid and base systems are detailed in Table 1. The system in Table 1 is assumed to have a CO₂ extraction capacity of 20 kmol(CO₂)/h. As shown in Part II (Eisaman et al., 2017), pairing IOC with a desalination plant can greatly reduce the cost of avoided CO2. Therefore we choose 20 kmol(CO2)/h as a system size as it represents the flow from a typical mid-size desalination plant. As also shown in Part II, however, in order to ultimately have a Gton(CO₂)/y impact, more expensive stand-alone plants will eventually need to be built and the optimum size for these may be > 20 kmol(CO2)/h, allowing somewhat decreased costs relative to our estimate due to increased scale of components. Details of our approach to sizing equipment to the 20 kmol(CO_2)/h scale based on the prototype measurements described in this paper can be found in the SI. While uncertainty is reduced by the fact that many of the unit operations are modular (i.e., scaling requires more units, not larger units) experimental tests of scaled unit operations are suggested prior to deployment of a 20 kmol(CO₂)/h system. It was determined that energy consumption was a critical cost associated with both the acid and the base systems (Eisaman et al., 2017). As Table 1 indicates, the greatest energy consumption occurs from BPMED. Further, approximately 40% more total energy is required using the base process than the acid process. This is primarily due to the increased base production required (produced by BPMED) for precipitation of CaCO₃ and for returning the brine alkalinity to its original level. Values of energy consumption of non-ED components come from manufacturer specifications. Values of ED energy consumption are based on the assumption of 95% faradaic efficiency, an electro-osmosis coefficient of 3.5, electronics efficiency of 98.5%, and a single-cell voltage of 2.85 V operating at $\sim 1000 \text{ A/m}^2$. For the calculation of avoided emissions in the concurrently published techno-economic analysis (Eisaman et al., 2017), we assume that all energy inputs into the IOC process are carbon-free. This is reasonable since the avoided CO₂ cost for new carbon-free electricity generation will likely remain cheaper than IOC and other NETs for some time. Therefore, IOC deployment will not be significant until the electricity grid is mostly decarbonized. This is a critical assumption, since the total electricity consumption values shown in Table 1, combined with an average U.S. grid emission factor of 5.59×10^2 t(CO₂)/GWh_e, results in more CO_2 being emitted than is captured.

The required membrane area for the best acid and base cases is shown in Table 2. While the base case needs substantially more electrodialysis due to the greater ratio of required moles of NaOH to

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Table 2

Membrane utilization for both electrodialysis and degassing, for acid and base best cases.

	Acid (best case, RO pair)	Base (best case, RO pair)
m ² ED membranes per tCO ₂ /day m ² membrane contactors per tCO ₂ / day	47 1340	71 0

captured CO_2 , the base case does not need membrane contactors at all, resulting in meaningful cost savings. Depending on the ultimate cost floor of these membranes, different system instantiations might be selected.

3.2. Electrodialysis current efficiency

The current efficiency of two membrane configurations were compared with each other: 1) AEM1-CEM1 and 2) AEM2-CEM1. The CEMs were the same for both configurations. These configurations are listed as AEM1-CEM1 and AEM2-CEM1 when discussing the acid production efficiency (anion dominated membrane interaction) and as CEM1-AEM1 and CEM1-AEM2 when discussing the base production efficiency (cation dominated membrane interaction). In each configuration, we measured the efficiency of the AEM membranes to produce acid and the CEM membranes to produce base, as a function of the acid concentration (0.22 N-2.17 N) and base concentration (0.26 N-2.35 N), respectively. The effect of changing brine concentration (2-20 wt%) was also studied. Fig. 4 presents the acid and base current efficiency data. These data have been corrected for the effect of electro-osmosis (details of this correction are presented in the SI and Fig. S5 shows the original uncorrected current efficiency data). The general trend for nearly all membranes in the BPMED system is that greater acid and base concentrations lead to lower respective membrane current efficiencies. The only set of data in which the trends are unexpected is that for the CEM1 membranes used in conjunction with the AEM2 membranes at high brine concentrations. This deviation is addressed in the Discussion. Some data points have > 100% current efficiencies. This is due to the electro-osmotic correction and error in measurements. This is discussed in detail in the SI.

Fig. 4 indicates that the efficiencies with which the AEM1 and CEM1 membranes in configuration 1 produce acid and base, respectively, were sensitive to the concentration of the acid and the base, based on the trend's slopes. Fig. 4 also demonstrates that the efficiencies with which AEM2 and CEM1 membranes in configuration 2 produce acid and base, respectively, are less sensitive to the concentration of acid and base, based on the trend's slopes. In both configurations 1 and 2, the efficiency of the AEM1 and AEM2 membranes was independent of brine concentration. The only evident outlier in the data was the seeming dependence of CEM1 membranes on high brine concentration in configuration 2, which is explained in the Discussion. The maximum achieved acid current efficiencies in configuration 2 (93.8%) are lower than those achieved in configuration 1 (98.3%), while the maximum achieved base current efficiencies in configuration 1 (107.3%) are approximately the same as those achieved in configuration 2 (108.6%). The base current efficiencies are reported as > 100% due to the electroosmotic correction, discussed in the detail in the SI. In sum, the AEM2 membranes have a broader range of applicability than the AEM1 membranes, but the AEM1 membranes may be able to achieve slightly higher current efficiencies at low concentrations. Finally, although the details are not shown here, it was determined that the current efficiencies obtained when using the AEM1, AEM2, and CEM1 membranes were independent of electrolyte concentration.

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Fig. 4. On the top is a comparison of the AEM1 [closed shapes] and AEM2 [open shapes] membranes' acid (HCl) production efficiency (%) as a function of average acid concentration. The AEM1 membranes are more sensitive to acid concentration than the AEM2 membranes. The order of the configuration name (eg. AEM1–CEM1) indicates that in acid production, Cl⁻ transport across the AEM1 membrane dominates the efficiency. On the bottom is a comparison of the CEM1 (with AEM 1) [closed shapes] and CEM1 (with AEM2) [open shapes] membranes' base (NaOH) production efficiency (%) as a function of average base concentration. The CEM1 membranes in configuration 1 (with AEM1) are more sensitive to base concentration than the CEM1 membrane is configuration 2 (with AEM2). The order of the configuration name (eg. CEM1–AEM1) indicates that in base production, Na⁺ transport across the CEM1 membrane is the focus of the efficiency determination. The Data point shapes (colors) indicate different brine wt% (circle 2 wt%, diamond 4 wt%, square 5.4 wt%, triangle 8 wt%, cross 20 wt%).

3.3. CO_2 extraction efficiency

The DIC concentrations of brine throughout the acid process were determined by TC/IC measurements and corroborated by extracted CO2 gas flow measurements, as detailed in the Methods section and in the SI. From the change in DIC concentration before and after CO₂ evolution, we determined the CO2 extraction efficiency for each membrane configuration (Fig. 3). Extraction efficiency is calculated as the concentration of carbon as CO₂, (calculated as mass of carbon stripped from the brine per volume of brine), per concentration of DIC available for extraction measured in the original brine (calculated as mass of carbon in the brine per volume of brine), passing across the total surface area of the CO2-extraction membranes at a given pressure. The total CO₂ that can be extracted from the brine is calculated by scaling the total DIC measured in the brine by the fraction of DIC that can form CO_2 . This is determined using the carbonate equilibrium at the measured pH of the brine. The surface area of each of the membrane modules is 1.4 m². This gives a figure of merit

mg of C in extracted CO_2

 $\{mg \ available \ C \ in \ brine\}\{m^2 \ membrane\}\{mbar \ applied \ vacuum\}$

with the appropriate correction subtracted from the denominator to account for the CO_2 solubility, and an efficiency simply represented by

Fig. 5. The CO₂ extraction efficiency/ m^2 from brine for each additional membrane (series configuration) [dotted lines, open shapes] or set of membranes (parallel configuration) [solid lines, solid shapes] connected in series. Each additional membrane or set of membranes have lower CO₂ extraction efficiency than the membranes before. Circles, Squares, and Triangles represent extractions at 30 mbar, 55 mbar, and 80 mbar vacuum pressure, respectively. The diminishing DIC removal efficiency for each additional membrane in series is due to the decreasing input DIC concentration for each additional membrane.

the ratio of $[mg \text{ of } C \text{ in extracted } CO_2]$ to [mg C in brine]. The average of all IC extracted at each pressure was calculated and compared.

CO₂ extraction with membranes in series is achieved by passing acidified brine through three configurations - 1, 2, or 3-as shown in Fig. 3. Similarly, CO₂ extraction with membranes in parallel is achieved by passing acidified brine through three configurations – 1×1 , 2×2 , or 3 \times 3-as shown in Fig. 3. Total CO₂ extraction efficiency for membranes in series and in parallel configurations, as well as CO₂ extraction efficiency per additional membrane module, are plotted in Fig. 5. Across all experiments, more CO₂ was extracted on an absolute basis, by increasing the number of membrane contactors or by applying a lower vacuum pressure. As a general trend across all experiments, each additional membrane contactor extracts less CO₂ than the one previous, i.e. an increase in the total number of membranes resulted in a lower CO2 extraction efficiency per membrane. As a general trend across all experiments, a lower vacuum pressure increases the CO₂ extraction, and thereby the CO₂ extraction efficiency, up to a minimum vacuum pressure of 30 mbar, although the differences in the efficiencies for each experiment were statistically insignificant. The errors bars are a result of averaging the data over multiple replicates of the same experiments. The total number of experiments performed per membrane configuration is detailed in the SI. All experiments were performed with brine. CO₂ extraction from ocean water using configuration 3×3 was performed and compared with that of brine in configuration 3×3 , and showed no change in extraction efficiency. This is discussed in detail in the SI.



Fig. 6. SEM image of crystalline CaCO₃ precipitate formed under controlled pH conditions.

3.4. Carbonate mineral precipitation

Controlling the pH of the solution allowed the selective precipitation of CaCO₃ without precipitation of Mg. White precipitate formation was first observed at pH 8.47, and precipitation continued with the continued addition of NaOH to < pH 9.6. In total 45.1 mg of NaOH was added to 200 mL of ocean water to precipitate out predominantly CaCO₃ from solution. As a comparison to the controlled precipitation of CaCO₃, the pH of brine was raised significantly above pH 10 to allow all precipitation (Mg(OH)₂, MgCO₃ and CaCO₃) to form. NaOH was added to the ocean water and white precipitate formed above pH 9–12.7. No precipitate was observed to form above pH 12.7.

The chemical composition of the precipitate formed at pH > 10 was compared with that formed between 9.3 < pH < 9.6. SEM images shown in the SI demonstrate the difference between the predominantly amorphous Mg(OH)₂ and MgCO₃ aggregates (precipitated at pH > 10) and the predominantly crystalline CaCO₃ (precipitated at 9.3 < pH < 9.6). A representative crystalline CaCO₃ structure is shown in Fig. 6 and the results of EDS measurements on both precipitates are listed in Table 3.

4. Discussion

4.1. Economic considerations

It is projected that the greatest individual costs to this negative emissions technology are electricity, electrodialysis (ED), and membrane contactors for the extraction of CO_2 gas. For an in-depth analysis of cost factors and sensitivities the interested reader is referred to the

Table 3

Distribution of elements in precipitates formed under rapid precipitation (pH $\,>\,$ 10) and controlled slow precipitation (9.3 $\,<\,$ pH $\,<\,$ 9.6).

Condition	Element	Weight%	Atomic%
pH > 10			
	Mg	23.35	15.90
	Ca	4.70	1.94
	0	44.78	46.32
	С	24.74	34.09
	Cl	-	-
	Na	2.43	1.75
9.3 < pH < 9.6			
	Mg	1.03	0.88
	Ca	33.59	17.53
	0	36.47	47.69
	С	13.47	23.47
	Cl	11.33	6.69
	Na	4.10	3.73

concurrent techno-economic analysis in this issue (Eisaman et al., 2017).

For the acid process, our cost model indicates that membrane contactors are a significant cost driver, and sensitivity to DIC concentration is observed because a lower DIC concentration requires more membrane contactor area per mole of CO₂ extracted; in the base process, no membrane contactors are needed, eliminating a significant capital expense. In the base process, carbon from CO₂ in the form of CaCO₃ can be sequestered by burying it, sinking it to the bottom of the ocean or potentially using it in building materials. Alternatively, HCl added to the CaCO₃ will evolve neat CO₂ gas (2HCl + CaCO₃(s) \rightarrow CO₂(g) + CaCl₂ + H₂O). In the acid process, CO₂ gas is directly generated.

In either process, absent a salable byproduct of either the $CaCO_3$ precipitate from the base process or the purified CO_2 gas from the acid process, it may be true that the base process can extract CO_2 at a lower overall cost than the acid process.

Electrodialysis and electricity consumption are closed inter-related: (a) it is projected that the cost of CO_2 is most sensitive to electricity price; and (b) ED is the unit operation with the highest electricity consumption. Since electricity for ED is a significant cost driver for both the acid and base processes, both processes are sensitive to the ED current efficiency. ED current efficiency measures how much electricity is required to generate an amount of HCl and NaOH. The current efficiency was shown to be highly dependent on the acid and base concentration. Further, higher acid and base concentrations reduce demineralized water demand, reducing the overall water treatment cost. Therefore, one impactful way to improve this negative emissions technology is to develop inexpensive and highly selective AEM and CEM membrane materials that can operate efficiently at higher acid and base concentrations. Because electrodialysis is a small industry today, there may be opportunity for significant improvement in membrane performance and decrease in cost.

It should be noted that in the absence of partnership with RO or power plant cooling, the dominant electricity consumption originates from the pumping and pretreatment of ocean water. In the case that a stand-alone plant was required, significant systems engineering would be needed to reduce this energetic expense.

4.2. Electrodialysis current efficiency

The primary result obtained from electrodialysis experiments is that the current efficiency of the ED process decreases with increasing acid and base concentrations in contact with the AEM and CEM membranes. This trend was shown to be consistent for acid and base current efficiency in all acid conditions and all but two base conditions (Fig. 4). This trend can be explained by considering the osmotic force in opposition to increasing acid and base concentrations and the increased coion transport of the membranes at high acid and base concentrations. Higher solute concentrations in the acid or base compartment result in a stronger osmotic flow of solvent (water) into the acid and base compartments. This counteracts increases in the acid or base concentration and reduces the current efficiency. In general, as solution concentrations increase and approach the charge densities of the AEMs and CEMs, the AEM and CEM permselectivities decrease. That is, the likelihood increases of co-ion transport of H⁺ through the AEMs and OH⁻ ions through the CEMs, thereby reducing current efficiency.

Furthermore, the seemingly counterintuitive dependence of NaOH production efficiency on the AEM type is explained by the increased coion transport of H^+ ions through the AEMs at higher solution concentrations. Once H^+ ions have entered the brine compartment via coion transport through the AEM, they can easily enter the neighboring base compartment via counter-ion transport across the CEM separating the brine and base compartments. Here the H^+ ion reduces NaOH production efficiency by neutralizing an OH^- ion. H^+ ions are an order of magnitude more mobile than OH^- ions, and therefore have a greater contribution to the variability in efficiency than other ions in the

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system. The only barrier to H^+ transport into the base compartment, and the corresponding reduction in NaOH production efficiency, is the permselectivity of the AEM.

The general trend of decreasing base current efficiency of the CEM1 (cation exchange membranes) for increasing base concentration, shown in the bottom panel of Fig. 4, holds for all brine conditions and configurations with the exception of 2 wt% and particularly 20 wt% brine in configuration 2 (CEM1–AEM2). This apparent deviation from the expected trend is a result of the electro-osmotic correction applied to the data for both cations and anions, and is attributable to a difference in the electro-osmotic force experienced by cations and anion. The difference in the trends in the unmodified data (Fig. S5) compared to the modified data (Fig. 4) suggests that the dynamics of base production at high base concentrations and high brine concentrations. Despite these two inconsistencies, the other conditions demonstrated consistent agreement that increasing acid or base concentration lead to decreasing acid and base current efficiency.

From Fig. 2, one would expect that the efficiency of acid production would be predominantly dependent on AEM membranes, while the efficiency of base production would be predominantly dependent on CEM membranes. In Fig. 4, however, it was observed that the base production efficiency with the same CEM (CEM1) was significantly affected by a different AEMs (AEM1 vs AEM2). This was evident in the large differences in the slopes of configuration 1 as compared to configuration 2 in Fig. 4 (bottom panel). An explanation is that changes to the permselectivity of the AEM cause more H⁺ to pass through the AEM. More H⁺ in the brine compartment easily pass the CEM and enter into the base compartment where they combine with OH⁻ to produce H₂O, thereby diluting the base and reducing the calculated base production efficiency. Further, H⁺ in the brine compartment (due to transport across the less permselective AEM) migrate more quickly than Na⁺ through the CEM leading to fewer Na⁺ crossing the CEM, thereby further reducing the base concentration and reducing the base production efficiency. This effect is augmented for greater NaOH concentrations in the base compartment. Specifically, if the concentration of Na⁺ is high in the base compartment, the osmotic pressure preferentially encourages the transport of H⁺ over further transport of Na⁺ from the brine compartment into the base compartment.

The impacts of changes to the AEM are clear from Fig. 4 in which the base current efficiency as measured with the CEMs in configuration 1 shows a steeper negative slope than the base current efficiency measured with the CEMs in configuration 2. From the above discussion, this implies that the AEM1 membranes are less permselective than the AEM2 membranes, and that AEM1 membranes cause greater H⁺ mobility into the brine compartment than AEM2 membranes. At high base concentrations, this in turn leads to the preferential transport of H⁺ from the brine compartment into the base compartment. This significant difference in slope implies that the AEMs have a significant effect on the base current efficiency at high base concentrations.

This analysis quantifies important metric benchmarks that must be met to enable real-world application.

4.3. CO₂ extraction efficiency

The total CO_2 extraction efficiency was shown to increase with longer residence time in the membrane contactor (either more modules in series, more modules in parallel, or lower flow rates), however the CO_2 extraction efficiency as a function of each additional membrane module showed diminishing returns. This trend is demonstrated in both panels in Fig. 5, which shows the efficiency for a brine solution with two times the DIC concentration of natural seawater; total extraction of CO_2 increases with more membranes in series (Fig. 5, top) but each additional membrane has a lower extraction efficiency (within experimental error) than the one previous (Fig. 5, bottom) due to the decreasing input DIC concentration being fed into each additional membrane. For the brine shown in Fig. 5, one membrane removes approximately 50–65% of the input DIC, while the second membrane only removes about 40–60% of the *remaining* DIC. Since brine has twice the DIC concentration as seawater, the DIC being fed into the second membrane in Fig. 5 has a DIC concentration close to that of seawater. This implies that a single membrane will remove 50–65% of the DIC in brine but only 40–60% of the DIC in seawater.

Overall, many factors are responsible for the limited CO_2 extraction efficiency. First, since each successive length of contactor (whether a longer contactor or simply more modules in series) removes a fixed fraction of the input concentration, increasing the length/number of contactors in series results in diminishing returns. On top of this, the mass transfer efficiency of the gas phase decreases as the gas concentration decreases, meaning that this constant removal fraction itself is decreasing with length. Finally, as seen in Fig. 5, by Henry's law the remaining (i.e., not extracted) gas concentration in the output solution is proportional to the partial pressure of CO_2 gas in the headspace of the membrane contactor. This CO_2 partial pressure is itself proportional to the vacuum level, resulting in smaller extraction efficiencies for higher vacuum levels (i.e., 80 mbar) compared to lower levels (i.e., 30 mbar).

However, the diminishing extraction efficiency of subsequent membranes indicates that by using more membranes the extraction efficiency for brine eventually becomes equivalent to that for seawater, enabling only twice as much CO_2 to be removed using brine over seawater. Indeed, an experiment was performed on seawater with membrane configuration 3×3 . The extraction efficiency for this experiment was identical to that using brine (details presented in Table S5 of the SI). Regardless of the membrane configuration, for a finite number of membrane contactors, more CO_2 can be removed from brine than from seawater, making it more economical to use brine than seawater for CO_2 extraction.

The difference in CO_2 extraction efficiency as a function of applied vacuum pressure at any membrane configuration was not statistically significant. This implies that a vacuum pressure of 80 mbar is sufficient to effectively and efficiently extract the maximum amount of CO_2 from the acidified brine, and lower pressures/higher vacuum (which is more expensive to achieve) do not provide any statistically significant benefit.

4.4. Carbonate mineral precipitation

The large difference in chemical composition of the two precipitates is due to the difference in precipitation dynamics between Mg(OH)2 and CaCO₃. CaCO₃ precipitates at a much slower rate than Mg(OH)₂, and CaCO₃ precipitation starts at a ~pH 9.3 as compared to Mg(OH)₂ precipitates that starts at > pH 9.6. Therefore, the controlled precipitation at 9.3 < pH < 9.6 predominantly produced CaCO₃ over Mg(OH)₂ while the precipitation at higher pH generated predominantly Mg(OH)₂ over CaCO₃. This assumption was supported by the EDX data. The mole ratio of O:C:Ca in the controlled 9.3 < pH < 9.6 precipitation was 2.7:1.3:1, suggesting that there was sufficient O and C in the precipitate to form CaCO₃ as the dominant species accounting for 100% of the total moles of O, 90% of the total moles of Ca, and 69% of the total moles of C in the precipitate. In the uncontrolled precipitation experiment, the precipitate had a mole ratio of O:C:Mg of 2.9: 2.1:1, suggesting that there was sufficient O in the precipitate to form Mg(OH)₂ as the dominant species accounting for 100% of the moles of Mg and 69% of the total moles of O. This experiment demonstrated that the selective precipitation of CaCO₃ is possible.

It should be noted that on a global scale of ocean de-carbonation, environmental mineral balance will be a concern as we are replacing Ca^+ with Na^+ to restore alkalinity. It is unclear if this would cause environmental or ecological impacts, and this should be considered in future base-process studies (Kirchofer et al., 2012).

5. Conclusions

Prototype assessment of the acid and base IOC systems, respectively, has provided critical information on the expected efficiency of this process, and provided experimental data for a concurrent real-world techno-economic analysis (Eisaman et al., 2017). BPMED accounts for approximately 80% of the total energy spent in capturing CO₂, making it the most critical component for efficiency optimization. Our measurements determined that BPMED current efficiency (i.e. acid/base production efficiency) was significantly greater for lower acid and base concentrations. However, lower acid and base concentrations require higher volumes of ocean water for the same mass of captured CO₂. Therefore, an economic trade-off exists between operating the BPMED at higher efficiency but requiring the treatment of more brine, and treating less brine but operating the BPMED at lower acid and base production efficiencies. The constraints on this trade-off could be relaxed by developing AEMs that can more effectively prevent proton leakage and thereby operate efficiently at higher acid (and base) concentrations, by developing a BPMED system that requires less input energy to produce the same concentration of acid and base, or by finding IOC system configurations that allow for more dilute operation without cost increases from the pre-treatment of brine.

 CO_2 extraction using the acid process indicated diminishing returns in net membrane contactor extraction efficiency as more membrane contactor modules are added. Fewer membranes extract less CO_2 from brine, requiring more ocean water to achieve the same amount of total CO_2 extracted. A trade-off exists between pumping less ocean water across more membrane contactors with cumulative lower CO_2 extraction efficiencies, and using fewer, and therefore more efficient, CO_2 extraction membranes but requiring pumping greater amounts of ocean water for de-carbonation. In addition, these experiments demonstrated that using a single membrane one can extract approximately three times as much CO_2 by using brine over ocean water, but due to diminishing returns, for more than three membranes in series one can only remove twice as much CO_2 by using brine over ocean water. This implies that opportunities for decarbonizing brine may enable higher process efficiency.

Lab-scale assessment of the base process indicated this to be an economically promising alternative to the acid process, due to its lack of expensive membrane contactors for CO_2 extraction. The base process merits more investigation into its potential cost reduction, requiring empirical information and an integrated prototype system to be built.

It is also important to ask what the impacts may be on the ocean ecosystem if these concepts are implemented at the few Gton(CO₂)/year scale relevant to climate change mitigation. Both the acid and base IOC processes would extract seawater from the mixed surface layer, which has an average depth 25 m-150 m, depending on location and season (Montegut et al., 2004). After CO₂ extraction, the decarbonized seawater with restored alkalinity would also be released back into the mixed surface layer to capture additional CO₂ from the atmosphere as it equilibrates with the atmosphere. In general, it takes about one year for the surface mixed layer to equilibrate with the atmosphere (Broecker and Peng, 1982). Dispersal of the decarbonized seawater with restored alkalinity back into the surface ocean would need to be carefully controlled, as the initial pH would be around 10.6 prior to equilibration. Absorption of atmospheric CO₂ would eventually bring the pH back to around 8.3, but the process design would need to avoid temporary, localized areas of high pH. Assuming an average DIC of 2.5×10^{-3} mol per liter, an average mixed surface layer depth of 50 m, and a global ocean area of 360×10^6 km³ (Lutgens, 1992), extracting 1 Gton(CO₂) per year from the mixed surface layer would only require processing five parts in ten thousand of this layer's global volume.

In summary, we have characterized the performance and identified key trade-offs in the systems design for indirect ocean capture systems. These results have been used to inform a concurrent techno-economic analysis of indirect ocean capture that appears in this same issue (Eisaman et al., 2017). Future technology improvements, such as ion exchange membranes that remain efficient at high acid and base concentrations, and process design choices, such as co-location with a desalination plant, are critical to improving the efficiency and lowering the cost of indirect ocean capture. IOC is a promising new negative emissions technology that could contribute to reducing atmospheric CO_2 levels. Although this prototype study has demonstrated that IOC is not economical in the near term, we have identified areas of research in which technological innovation and optimization can greatly reduce the overall costs. Further, it is hoped that this prototype study will shed light on the realistic costs associated with negative emissions technologies, and the fully integrated engineering analyses required to assess the areas of greatest cost.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ijggc.2017.10.007.

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