Biocement from the ocean: Hybrid microbial-electrochemical mineralization of CO₂

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SUMMARY

Increasing concentrations of atmospheric CO₂ are leading to rising global temperatures and extreme weather events. However, the most prominent method of removing CO₂ via direct air capture remains cost-prohibitive. Oceans sequester carbon through several naturally occurring carbon dioxide removal (CDR) processes, one of which includes microorganisms that utilize dissolved inorganic carbon (DIC) in their metabolic processes. Atmospheric CO₂ is in dynamic equilibrium with DIC at the ocean’s surface. Thus, ocean-based CDR can function to capture carbon from the air indirectly. This work discusses a hybrid method that combines primary CO₂ capture via the growth of autotrophic microorganisms (i.e., photosynthetic cyanobacteria) and microbially induced carbonate precipitation. Carbon fixation and carbonate precipitation can be co-optimized using bipolar membrane electrodialysis (BPMED) devices, which generate seawater with an adjustable pH. We examine the scale-up potential for naturally produced bio-carbonate composite material and compare its production with published ocean CDR strategies for reducing anthropogenic CO₂ emissions.

INTRODUCTION

Increasing atmospheric CO₂ levels have led to an enhanced greenhouse effect, rising global temperatures, and more extreme weather (Fischer et al., 2021). Currently, the atmospheric concentration of CO₂ has reached 421 ppm, an increase of more than 10% since the start of the century. In order to reach the goals set by the Paris Agreement to curtail anthropogenic carbon emissions and limit the global temperature rise to 1.5°C–2°C, negative emissions technologies (NETs) are necessary for the transition toward sustainable energy and chemical production processes (National Academies of Sciences and Medicine, 2019). Thus, there is an ever-growing need to explore CO₂ capture and conversion methods that are not only efficient but also economically viable (Hepburn et al., 2019).

The ocean is the world’s largest natural CO₂ sink, with an uptake rate of 2.5 gigatons per year, containing approximately 38,000 gigatons of carbon (Friedlingstein et al., 2020). Owing to its surface area, salinity, and alkalinity, the ocean plays a critical role in sequestering atmospheric CO₂, capturing roughly a third of current anthropogenic carbon emissions (DeVries, 2014). The concentration of inorganic carbon stored in the ocean is two orders of magnitudes higher than the amount in the atmosphere (Adams and Caldeira, 2008; Friedlingstein et al., 2020), and as separation costs scale with dilution, ocean-based carbon capture presents a promising alternative to direct air capture (DAC) (House et al., 2011). Naturally occurring forms of ocean capture include deep ocean storage (Royal Society, 2018), coastal blue carbon (Duarte et al., 2013; McLeod et al., 2011), and carbon mineralization such as basalt capture (Matter et al., 2016; Snæbjörnsdóttir et al., 2020). In addition, coupling ocean capture with the generation of value-added products can offset the cost of carbon capture and provide an economic incentive for negative emission technologies (Hepburn et al., 2019).

Dissolved inorganic carbon (DIC) at the ocean’s surface is in dynamic equilibrium with atmospheric CO₂. Continuous DIC removal would allow for the ocean to continuously uptake CO₂ from the air, providing an alternative to direct air capture. The pH-swing process leverages the ocean’s pH-dependent CO₂-bicarbonate-carbonate equilibrium to remove DIC from the ocean. In a demonstration by Eisaman et al., the pH-swing method was used to extract 59% of the total DIC from synthetic seawater in the form of gaseous...
CO\textsubscript{2}. This process consumed 242 kJ of electrochemical energy per mol of CO\textsubscript{2} (5,499 MJ per metric ton of CO\textsubscript{2}) (Eisaman et al., 2012). However, the CO\textsubscript{2} was removed by gas stripping, thus requiring further sequestration or utilization of gaseous CO\textsubscript{2}. Recently, a similar vacuum stripping process was coupled with electrochemical CO\textsubscript{2} reduction, utilizing the captured CO\textsubscript{2} to generate value-added chemicals from simulated seawater (Digdaya et al., 2020).

Thus far, electrochemical ocean CDR has been characterized as either acidic or alkaline capture (Table 1). A transition to lower pH shifts the equilibrium toward the right side of Equations 1a and 1b, converting soluble carbonate and bicarbonate into dissolved gaseous CO\textsubscript{2}, which can be extracted and later transported. The pH shifts toward its original value following CO\textsubscript{2} removal, thus minimizing ocean acidification. Additionally, lowering the pH can also accelerate the rate of weathering, the process where carbonate and silicate minerals are dissolved via acid-base reactions to increase alkalinity, further mitigating ocean acidification (Hartmann et al., 2013; Rau et al., 2013).

\[
HCO_3^- (aq) + H^+ \rightleftharpoons H_2O + CO_2(g) \quad \text{(Equation 1a)}
\]

\[
CO_3^{2-} (aq) + 2H^+ \rightleftharpoons H_2O + CO_2(g) \quad \text{(Equation 1b)}
\]

Conversely, a transition to higher pH leads to the supersaturation of dissolved carbonate species, allowing DIC removal through the precipitation of solid calcium carbonates (Equation 2), magnesium carbonates, dolomite, and silicate minerals (Bénézeth et al., 2018; Kline, 1929; Mucci, 1983; Renforth and Henderson, 2017; Stefansson, 2001). The driving force of calcium carbonate (i.e., calcite) precipitation strongly depends on pH. This precipitation process should not be confused with alkaline mineralization, where CO\textsubscript{2} dissolved in the ocean reacts with the existing basaltic rocks (containing CaO and MgO) or silicate minerals to form carbonates (Equations 3 and 4) (Lackner et al., 1995; Matter et al., 2016; Rau et al., 2013; Romanov et al., 2015). Naturally, this process is a part of global biogeochemical cycles and can be accelerated with an engineered solution (Rotmans and Elzen, 1999).

\[
HCO_3^- (aq) + Ca^{2+} + OH^- \rightarrow H_2O + CaCO_3 (s) \quad \text{(Equation 2)}
\]

\[
(Ca, Mg)O(s) + CO_2(g) \rightarrow (Ca, Mg)CO_3 (s) \quad \text{(Equation 3)}
\]

\[
(Ca, Mg)SiO_3 (s) + CO_2(g) \rightarrow (Ca, Mg)CO_3 (s) + SiO_2(s) \quad \text{(Equation 4)}
\]

Calcite precipitation is both kinetically and economically challenging (Spanos and Koutsoukos, 1998), even though untreated ocean water is supersaturated with carbonates (more than double the amount found in pure calcium carbonate solutions) (Ca et al., 2007). This steady-state supersaturation is due to the presence of other chemical species (i.e., Mg\textsuperscript{2+}, SO\textsubscript{4}\textsuperscript{2-}, and inorganic phosphates) in the ocean. These dissolved species inhibit spontaneous inorganic calcium carbonate precipitation and growth (Morse et al., 2007; Nielsen et al., 2016; Pytkowicz, 1965, 1973). However, calcium carbonate precipitation can also occur through biogenic means. Many marine organisms utilize the supersaturated calcium and carbonate species in the ocean to grow carbonate-based structures or complexes via biological processes (Achal et al., 2015).

Microbially induced carbonate precipitation (MICP) is a novel method of accelerating precipitation by introducing biological or microorganism-derived nucleation seeds (Castro-Alono et al., 2019). The predominant mechanisms of nucleation are under active investigation. The proposed mechanisms include 1) cellular metabolism, where negatively charged metabolites are excreted from the cell, generating a locally alkaline environment; 2) electrostatic interactions, where a negatively charged cell membrane attracts positively charged calcium ions, creating a local driving force. Cyanobacteria are a class of marine microorganisms that fix carbon during the day and excrete it at night—serving as both a source and sink of CO\textsubscript{2}. Optimal cyanobacteria growth occurs at elevated pH values between 7.5 and 10 (Fogg, 1956). Cyanobacteria have inhibited growth at lower pH values and generally cannot grow in environments with pH values below 4–5 due to an insufficient concentration of bicarbonate, their preferred substrate, at this pH range (Brock, 1973; Fogg, 1956). These bacteria, if engineered to better tolerate acidic environments, could utilize the increased amount of dissolved CO\textsubscript{2} to accelerate their population growth.

Coordinating acidic and alkaline capture presents a unique opportunity to harness the merits of CO\textsubscript{2} stripping and inorganic precipitation while overcoming the individual limitations of both. This hybrid approach can benefit from engineered solutions such as co-optimizing the pH of seawater media for CO\textsubscript{2}-fixing
| Strategy                                           | Acid/Alkaline CO₂ Capture | Feed/Input          | Energy Consumption (kJ mol⁻¹ CO₂) | Key Features/Concerns                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | References                  |
|---------------------------------------------------|---------------------------|---------------------|----------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------|
| BPMED + vacuum                                    | Acid                      | Artificial seawater | 242                              | 59% of the total DIC extracted from seawater; CO₂-depleted acid solution recombined with a basified solution to produce neutral-pH solution.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | (Eisaman et al., 2012)      |
| BPMED + vacuum                                    | Acid                      | Synthetic seawater  | 155.4                            | 71% CO₂ capture efficiency; CO₂ reduction cell converts captured CO₂ into fuels and chemicals; Reversible redox-couple solutions reduce unintended electrode reactions and electrochemical energy consumption.                                                                                                                                                                                                                                                                                                                                                                                                  | (Digdaya et al., 2020)      |
| Electrolytic cation exchange module + vacuum     | Acid                      | Natural seawater    | Not reported                     | Degassed and recovered 92% of CO₂ from seawater; Acidified seawater is recombined with the basified solution to return the effluent to the original pH, and polarity reversal minimizes mineral scaling and deposition.                                                                                                                                                                                                                                                                                                                                                                     | (Willauer et al., 2014)     |
| Enhanced weathering via electrochemical HCl removal | Alkaline                   | None                | 100-400                          | Net reaction/process is essentially identical for seawater or artificial brine; Process operates on geological time scales; Seawater feed leads to membrane, electrode, and diaphragm clogging/fouling; Scaling limitations and challenges.                                                                                                                                                                                                                                                                                                                                                                           | (House et al., 2007)        |
| Electrolytic calcium carbonate splitting          | Alkaline                   | Natural seawater    | Not reported                     | Produces hydroxide solutions without thermal calcination or electrochemically NaCl splitting; The experimental cell configuration used was not thermodynamically optimized; Cathodic carbonate and hydroxide precipitation may impact electrolytic cell performance.                                                                                                                                                                                                                                                                                                                                                                                           | (Rau, 2008)                 |
| Enhanced weathering via electrolytic dissolution of silicate minerals | Alkaline                   | Na₂SO₄/deionized water solution | 426-481                          | Precipitation of silica or other sulfates on an anode may reduce conductivity over time; Precipitating metal carbonates from metal derived from mineral silicates was not demonstrated.                                                                                                                                                                                                                                                                                                                                                                                                     | (Rau et al., 2013)          |
| Strategy                                      | Acid/Alkaline CO₂ Capture | Feed/Input                                      | Energy Consumption (kJ mol⁻¹ CO₂) | Key Features/Concerns                                                                 | References                        |
|----------------------------------------------|---------------------------|-------------------------------------------------|----------------------------------|--------------------------------------------------------------------------------------|-----------------------------------|
| Microbial electrolytic carbon capture        | Alkaline                  | Artificial and real wastewater\(^a\)            | 57–62 net energy gain            | 80%–93% of CO₂ generated or artificially injected was captured; H₂ recovery and yield rate of 91%–95% and 75%–76%, respectively; Potential fouling problems need to be further studied; Recalcitrant substrates in wastewater inhibit continued biodegradation. | (Lu et al., 2015)                  |
| BPMED + brine input                          | Alkaline/Acid             | Approximately 394 and 658 for the acid and base process, respectively\(^i\) | More CO₂ was extracted by increasing the number of membrane contactors or by operating at a lower pressure; BPMEDs are responsible for ~80% of total energy consumption. |                                                     | (de Lannoy et al., 2018)          |

\(^a\)NaCl-NaHCO₃/deionized water solution and sea salt/deionized water solution.
\(^b\)Sea salt/deionized water solution.
\(^c\)Seawater from Key West, FL.
\(^d\)Total work calculated across a range of efficiencies scenarios and time scales.
\(^e\)To offset 15% of carbon annual carbon emissions, 10¹⁴ mol of HCl needs to be removed annually and will require ~100 plants with capacities of large sewage faculties.
\(^f\)Local seawater from Santa Cruz, CA.
\(^g\)Energy consumption was >10³ higher than expected.
\(^h\)Real wastewater collected from a hydraulically fractured shale gas well in Piceance Basin, CO.
\(^i\)Calculated assuming a CO₂ extraction rate of 7202 metric tons of CO₂ per year and energy consumption of 17.9 and 29.9 GWh for the acid and base process, respectively.
microorganisms in the acidic medium and maintaining the pH at 9.3 ensures selective precipitation of carbonates over hydroxides in the alkaline medium. A previous study reported that 225.5 mg of NaOH was necessary to remove all the DIC from 1 L of seawater (de Lannoy et al., 2018). The techno-economic analysis of this process showed that the majority of the cost stemmed from the use of NaOH as the alkaline agent.

Instead of adding a base, electrodialysis driven by renewable energy can replace the necessity for a costly stoichiometric input, e.g., NaOH (Eisaman et al., 2018). Recent advances in bipolar membrane (BPM) development with the potential to create cost-effective alkaline seawater media were not considered in the previous analysis.

Inspired by nature, we envision a process that allows for independent optimization of organic growth and inorganic carbonate precipitation. Our system combines the scalability of MICP with the on-demand pH control afforded by an efficient BPM electrodialysis system to capture oceanic CO₂ indirectly. This hybrid microbial-precipitation approach would allow CO₂ to be individually and simultaneously extracted from an acidified and a basified media, while generating a product of carbon-rich materials and an output waste stream of seawater with sufficient alkalinity and salinity (Figure 1). The organic and inorganic carbon composition of the “biocement” product can be tuned based on the flow rate and pH. The carbonate compositions in the biocement and regular cement are similar. This approach removes the risk of introducing material that could adversely affect the ocean’s ecosystem, a concern that alkaline mineral weathering solutions must overcome (Bach et al., 2020; Hartmann et al., 2013). Meanwhile, this process creates low-carbon materials, i.e., biocement, as a potential alternative to the construction sector. To that end, we recommend independent process development at optimized pH and throughput followed by the coordination of the two processes into a hybrid natural-and-engineered negative emission solution.

CARBONATE EQUILIBRIUM AND OCEAN GEOCHEMISTRY

Direct air capture (DAC) requires sorbents capable of separating parts per million (ppm) level CO₂ and thus must have a strong binding affinity for CO₂. This binding affinity necessitates energetically intensive regeneration of the dilute CO₂ capture media. This cost can be circumvented when utilizing indirect ocean capture because the dissolved inorganic carbon (DIC) concentration in the ocean is higher than the ~420 ppm CO₂ in the air. CO₂ in seawater exists mainly in the form of bicarbonate (HCO₃⁻), the primary constituent...
of DIC. Typically, seawater has Ca$^{2+}$ and DIC concentrations around 10.5 and 2 mM, respectively. The solubility limit of CaCO$_3$ in typical seawater at pH ≥ 10 is only 0.047 g/L (0.47 mM), almost an order of magnitude smaller than the concentration of DIC. Under such pH conditions, this degree of oversaturation leads to an appreciable driving force for CaCO$_3$ precipitation.

Precipitation (MICP) is controlled by four key factors: calcium concentration, DIC concentration, pH, and the availability of nucleation sites. The calcium concentration, DIC concentration, and pH have a direct influence on the thermodynamics of calcium carbonate precipitation. The calcite saturation state is used to measure the state of supersaturation (Equation 5) (Gebrehiwet et al., 2012; Renforth and Henderson, 2017).

$$\Omega_{\text{calcite}} = \frac{\alpha_{\text{CO}_3^2^-} \cdot \alpha_{\text{Ca}^{2+}}}{K^c}$$  
(Equation 5)

$\Omega_{\text{calcite}}$ is the ratio of the ion activity product of CO$_3^{2-}$ and Ca$^{2+}$ and the temperature-dependent solubility product constant, represented by $\alpha_{\text{CO}_3^2^-}$, $\alpha_{\text{Ca}^{2+}}$, and $K^c$, respectively. The ion activity product is influenced by the presence of other ionic species, quantitatively represented by practical salinity, $S$ in Equation 6 (Renforth and Henderson, 2017).

$$\alpha_{\text{CO}_3^2^-} \cdot \alpha_{\text{Ca}^{2+}} = \frac{K^c}{K^c} \left( 1 - \frac{S}{1000} \right)^2$$  
(Equation 6)

Classical nucleation theory defines the precipitation driving force by the total change in chemical potential for nucleus formation, $\Delta G$ (Equation 7) (Cao, 2004; Karthika et al., 2016).

$$\Delta G = -V_{\text{nucleus}} \cdot \frac{k_B T}{V_{\text{atomic}}} \ln(\Omega_{\text{calcite}}) + \Delta \mu_s$$  
(Equation 7)

For precipitation to occur at an appreciable rate, the solution must be highly supersaturated, meaning $\Omega_{\text{calcite}} \gg 1$. At pH 9.30, $\Omega_{\text{calcite}}$ is ~30. Cyanobacteria cell surfaces and the exopolysaccharides they produce have negative surface charges that attract calcium ions, making them ideal nucleation and precipitation sites (Kamennaya et al., 2012; Vahabi et al., 2013). As Ca$^{2+}$ ions migrate toward the negatively charged surfaces, $\Omega_{\text{calcite}}$ increases in the surrounding solution layer, increasing the precipitation driving force and accelerating the CaCO$_3$ precipitation (Kamennaya et al., 2012). It has been demonstrated that the combined catalyzing mechanisms of cyanobacteria are roughly equivalent to an 18% reduction in the specific interfacial free energy, $\Delta \mu_s$ (Obst et al., 2009).

**BIPOLAR MEMBRANES DIALYSIS FOR TUNING ALKALINITY IN REAL TIME**

Bipolar membranes (BPMs) consist of two laminated layers of an anion exchange layer (AEL) and a cation exchange layer (CEL). The AEL material has fixed cationic groups, which interact with mobile anions electrostatically, and vice versa for the CEL. The junction of these two layers is known as the interfacial layer (IF), where water dissociation or H$^+$/OH$^-$ recombination can occur, depending on the applied bias. During electrodialysis, the electric field produced from the applied potential drives H$^+$ ions produced from water dissociation away from the IF through the CEL. At the same time, OH$^-$ ions are driven through the AEL, creating a steady-state pH difference across the membrane (Oener et al., 2020). Simultaneously generating an acidic and a basic environment makes the BPM electrodialysis (BPMED) devices suitable for subsequent acidic or alkaline carbon capture approaches. Additionally, catalysts can be incorporated into the IF to improve reaction rate and catalytic efficiency (Oener et al., 2020).

The BPMED system in the envisioned process utilizes a four-compartment BPM electrodialysis flow cell to generate acidified and basified streams from natural seawater (Figure 2). A reversible redox-couple solution is recirculated between the two outer chambers and is separated from the seawater chambers by CELs. The ocean water passes through two inner chambers that are separated by the BPM. The primary energy loss in this BPMED process is the overpotential per ionic current passed through the BPM. Often, BPMs have been configured to take advantage of hydrogen and oxygen evolution reactions at the cathode and anode, respectively, and produce hydrogen fuel to offset operating costs (Willauer et al., 2011). However, these systems are constrained by substantial overpotentials required to drive the necessary current. Utilizing reversible and fast electron-transfer redox-couple solutions in the electrode chambers can reduce the overall energy consumption for CO$_2$ removal by preventing side electrode reactions (Djidaya et al., 2020). Redox couples need to have good solubility, low toxicity, and have limited mass transfer into or from the other compartments. Good examples include Fe(III)-EDTA/Fe(II)-EDTA, FeCl$_2$/FeCl$_3$ in a NaCl...
or Na₂SO₄ bulk solution, and [Fe(CN)₆³⁻]/[Fe(CN)₆⁴⁻] (Jang et al., 2020; Scialdone et al., 2012; Veerman et al., 2010). Electrodialysis electrodes need to be conductive, mechanically strong, demonstrate high pH stability, and be electrochemically inert (Jang et al., 2020; Scialdone et al., 2012; Veerman et al., 2010). As a result, electrodes such as platinized titanium and carbon, noble-metal-coated titanium mesh, graphite, and metal-oxides (e.g. Ru-Ir) have been employed (Jang et al., 2020; Veerman et al., 2010).

Membrane degradation is the primary durability limitation for BPMED. For example, the continuous mineral build-up may lead to membrane scaling, blocking membrane pores, increasing membrane resistance, and consequently reducing the energy efficiency of dialysis (Wang et al., 2011). If the cathode is in direct contact with seawater, pH swing-induced precipitation may occur and reduce electrodialysis performance (Rau, 2008). If not addressed, both issues necessitate eventual replacement of the membranes or electrodes, drastically increasing the operating costs of a scaled-up BPMED system. However, scaling at either the electrode or membrane is not a major concern in this system because the primary pathway of carbonate precipitation is through the indirect MICP process rather than through the direct addition of acid or base. In other words, MICP removes the need for carbonate precipitation to occur within the BPMED flow cell. The implementation of reversible redox-couple solutions prevents precipitation at the electrodes as the seawater is not in direct contact with the electrodes.

Developing novel strategies to prevent or reverse membrane degradation is imperative for their device applications in CO₂ capture and utilization. One method of further mitigating potential membrane scaling is implementing polarity reversal to dissolve the carbonate scaling. During the polarity reversal, the applied potential between the two electrodes is reversed, promoting H⁺ and OH⁻ recombination to form water. The recombination reaction causes the pH at the membrane’s surface to revert to its initial value, allowing carbonate scales to dissolve. The reversed direction of the electric field also causes other scales, such as silicates, to detach from the membrane surface (Lee et al., 2012; Willauer et al., 2014). In addition, hydrophobic coatings and modifying the membrane’s surface charge have also been investigated for mitigating membrane scaling. For example, coating ultrathin TiO₂ layers on the order of single nanometers has been demonstrated to impart resistance against chemical corrosion without damaging the membrane structure and functionality (Zhou et al., 2018).

**HYBRID MICROBIAL-ELECTROCHEMICAL CARBON CAPTURE AND UTILIZATION**

We envision a three-component microbial-electrochemical system that utilizes BPMED technology and MICP for energy-efficient carbon capture and utilization. The system, illustrated in Figure 3, consists of a...
bipolar membrane electrodialysis flow cell that generates acidified and basified seawater. The acidified and basified streams are fed as inputs for the photobioreactor and precipitation reactor operating in parallel, respectively. The cyanobacteria grown in the photobioreactor are separated from the photobioreactor outlet stream and fed into the precipitation reactor to serve as nucleation seeds for MICP.

Natural seawater is pumped into the two chambers of the BPMED flow cell. When a potential is applied, water dissociation at the BPM’s interfacial layer and subsequent ionic migration drives $\text{H}^+$ and $\text{OH}^-$ across their respective membranes, leading to simultaneous acidification and basification of seawater. The pH-manipulated acidified and basified streams then exit the flow cell separately, with the acidified stream for cyanobacteria growth and the basified stream for MICP. MICP occurs later with the cyanobacteria grown utilizing DIC in the acidified stream. The rate of $\text{H}^+$ and $\text{OH}^-$ generation in a BPMED device is proportional to the electrochemical current that drives water dissociation. Accordingly, the residence time of a flow cell is inversely proportional to the volumetric flow rate of incoming seawater. This means that the rates at which $\text{H}^+$ and $\text{OH}^-$ are added into the acidified and basified stream, respectively, are independently tunable. The pH of the acidified and basified seawater streams can also be tuned individually by having natural seawater entering the two chambers at different volumetric flow rates. Therefore, the pH of resultant seawater streams can be controlled independently (Digdaya et al., 2020). For example, increasing the flow rate will effectively dilute the seawater stream under an applied potential and vice versa. Modifying the applied potential and seawater flow rates allows for real-time pH tunability and potentially minimizes total energy consumption by co-optimizing pumping and electrodialysis.

In alkaline conditions, dissolved carbonate species become supersaturated, and by operating within the pH range of 9.3–9.6, $\text{CaCO}_3$ is selectively precipitated over $\text{Mg(OH)}_2$ (de Lannoy et al., 2018), thus maintaining the alkalinity of $\text{Mg}^{2+}$. The basified seawater stream is supersaturated with $\text{CaCO}_3$ for MICP, e.g., $\Omega_{\text{Calcite}} \approx 30$, with the cyanobacteria previously grown serving as nucleation seeds (Achal and Mukherjee, 2015; Achal et al., 2015). Microalgae cells culture are suspended in the carbon fixation photobioreactor in a batch process. Once the culture either reaches a critical density or a hold-up time, the culture is separated from the photobioreactor and transferred to the MICP reactor for precipitation. Many mature separation techniques, including centrifugation, filtration, and settling, are suitable. The precipitated product, “biocement”, will be separated from the basic seawater stream via sedimentation and filtration (Achal et al., 2015). The photobioreactor and MICP reactor exit streams are recombined to neutralize the effluent before discharging the effluent back into the ocean.
Table 2 lists the seawater parameters of each input and output stream in the simplified flow chart, as shown in Figure 3. Two master variables out of the three parameters, DIC, alkalinity (both in the units of mmol/kg seawater), and pH, determine the output stream parameters based on the equilibrium calculations using the PyCO2SYS library (Humphreys et al., 2022). The acidified and basified streams follow a fixed ratio based on the target pH of the acid and base streams of 7.5 and 9.3, respectively. The cyanobacteria growth rate (mass time$^{-1}$) is an external input to the model chosen to represent appreciable DIC removal via photosynthesis corresponding to a 62.6% decrease in DIC across the photobioreactor (streams 2 and 4). A bioaccumulation rate (the space-time growth rate in the photobioreactor) of 1 g L$^{-1}$ day$^{-1}$ was used as a reasonable growth rate based on literature (Kumar et al., 2011; Ludwig and Bryant, 2012; Włodarczyk et al., 2020) to calculate the size of the photobioreactor required for a given growth rate. Based on the empirical formula for Synechococcus sp. PCC 7002 (Beck et al., 2018), 0.5012 g of DIC is fixed per 1 g of cyanobacteria growth. Therefore, the organic carbon production rate, $r_{OC}$, equivalent to DIC consumption rate by cyanobacteria, in mol/kg seawater is

$$r_{OC} = \frac{(0.5012r_{\text{cyano}})}{M_C V_{\text{cyano}}}$$

where $r_{\text{cyano}}$ is the rate of cyanobacteria growth in g s$^{-1}$, $M_C$ is the molar mass of carbon 12.011 g mol$^{-1}$, and $V_{\text{cyano}}$ is the volumetric flow rate through the photobioreactor in kg s$^{-1}$. We reasonably assumed that CaCO$_3$ precipitation rate is related proportionally to cyanobacteria organic carbon on a molar basis such that:

$$\frac{r_{OC}}{r_{\text{CaCO}_3}} = 2.0$$

where $r_{\text{CaCO}_3}$ is the MICP rate with the unit of g s$^{-1}$. This value is in between a theoretical molar ratio of 1 based on the metabolic pathway for cyanobacterial MICP and experimental data for other calcifying cyanobacteria (Bundeleva et al., 2016; Martinho de Brito et al., 2022).

Due to the decrease in alkalinity, concerns may arise regarding CO$_2$ capture efficacy because there are reports that microbial calcification in the ocean results in a net increase of CO$_2$ in the atmosphere (Ware et al., 1992). As Ca$^{2+}$ is consumed during calcium carbonate precipitation, electrochemically generated hydroxides are also consumed, leading to a decrease in the seawater’s alkalinity (Equation 8), which is proportional to its buffer capacity. Despite the decrease in alkalinity due to carbonate precipitation consuming Ca$^{2+}$, cyanobacterial MICP should not cause the ocean to release CO$_2$ into the atmosphere. Inorganic carbon mineralization combined with photosynthetic cyanobacteria growth leads to DIC removal that is greater than the loss of CO$_2$ efficacy stemming from alkalinity consumption. In the case of Table 2, the resulting effluent seawater has a pH of 9.35. However, the effluent stream may need to be diluted with more seawater before discharge to decrease the pH to less than 9 in order to adhere to EPA guidelines (C.F.R., 2022). This alkaline CO$_2$-depleted seawater effluent can further uptake atmospheric CO$_2$ and aid in neutralizing ocean acidification. In other words, the mineral restoration process is optional because the ocean effluent shall not negatively impact the ocean geochemistry and marine ecosystem (Committee on... et al., 2021).

**DEMONSTRATIONS OF MICROBIAL GROWTH AND CARBONATE PRECIPITATION**

Dense cyanobacterial blooms are known to rapidly deplete dissolved CO$_2$ concentrations in eutrophic surface waters (Ji et al., 2017). Cyanobacteria rely on both light and CO$_2$. Many marine cyanobacteria have been studied extensively in the laboratory environment, so for this discussion, we will focus on a single
cellular strain (Synechococcus sp. PCC 7002) and a filamentous strain (Trichodesmium). Both strains are chosen because they both perform photosynthesis in the pH range of 8.5–10.0 optimally, and they have developed metabolic capabilities to ensure their survival in nutrient-depleted environments. It has been demonstrated that Trichodesmium can grow in iron- or phosphorus-limited environments while still engaging in nitrogen-fixing metabolic processes (Walworth et al., 2018). In artificial seawater, Trichodesmium has a doubling time of approximately 64.4 h (D = 0.01 h⁻¹) (Gardner and Boyle, 2017). Despite Trichodesmium’s lean-nutrient advantage, Synechococcus’s growth is far faster under continuous light with optimal medium composition, having a doubling time as low as 2.6 h when grown in a nutrient-rich artificial seawater medium (relative to the natural seawater) (Ludwig and Bryant, 2012). Since cyanobacteria tend to prefer growth in a slightly alkaline environment, transferring cyanobacteria to a higher pH environment is not expected to impact cell viability or growth significantly. This adaptation enables high-density cultures to be grown and then transferred to a more alkaline environment for continuous microbially induced carbonate precipitation.

CONSIDERATIONS FOR MICP PROCESS SCALE-UP

The proposed microbial-electrochemical process lends itself toward modular design and scale-up, given its flexible design and non-reliance on specialized equipment. The biggest concern in the design of this system is the washout. Washout is when the dilution rate, D = F / V, where F is the flow rate and V is the volume of the photobioreactor, is larger than the growth rate of the organism. Cyanobacteria have much slower growth rates compared to heterotrophic bacteria, especially when grown in nutrient-limiting media, such as seawater (Gardner and Boyle, 2017). However, in a fully replete medium, fast-growing cyanobacteria such as Synechococcus elongatus UTEX 2973 have been reported to double in as little as 1.9 h (D = 0.36 h⁻¹) (Yu et al., 2015). This is a key design feature and can easily be achieved (even in the slower growth case) by increasing the size of the photobioreactor. Growth can also be modified by adjusting the media. The most cost-effective approach would be to use seawater without nutrient supplementation, which is a viable option given that marine cyanobacteria have evolved to thrive in nutrient-depleted conditions. Should a faster growth rate be required, desired strains can be fully characterized to optimize nutrient supplementation to achieve the desired density. Any changes in nutrient concentrations from influent seawater must be appropriately measured such that the net community impact of the changes can be properly included in the carbon accounting of the process (Gallagher et al., 2022). Marine organism growth is typically limited by nitrogen, phosphates, or iron. Alternatively, cyanobacteria growth could be a batch process with diurnal solar cycles, which would mean that the volumetric flow rate of the acidified stream would follow a varying pattern to match the bicarbonate consumption rate. The rates of basified seawater and the microbial seed introduction can be tuned to match the carbonate precipitation rate.

It is essential to also consider the environmental impact of the as-described process. Due to the depletion of Ca²⁺ cations via precipitation, there is a decrease of Ω_{arag} between the influent and effluent streams of 0.65 which is almost equivalent to the ~0.7 decrease in Ω_{arag} observed from pre-industrial times to 1998 (Albright et al., 2016). Note that these saturation states are for aragonite, which nucleates preferentially over calcite following Ostwald’s rule of phases, and are both stoichiometric, not taking into account the activity constants for Ca²⁺ and CO₃²⁻ (Mucci, 1983). As the calcification rates of many calcifying organisms depend on the degree of supersaturation, this may negatively affect calcifying marine organisms and local ecosystems (Doney et al., 2009). Therefore, the implementation of this process would need to be sited carefully. Eventually, the effluent stream is diluted into ocean’s surface; since calcium is about 5 times more concentrated in seawater than DIC and there is only a 6% decrease in calcium concentration between the influent and effluent streams, the as-described process can be scaled to significant quantities of carbon removal without there being a significant change in calcium concentrations. Therefore, it is unlikely that there would be a large impact globally on calcifying organisms. Extensions of this process that include a method for alkalinity regeneration can be concealed. For example, alkalinity could be regenerated in the process by the removal of the electrochemically co-produced protons in the acidic stream as dilute hydrochloric acid (Sharifian et al., 2022) or by their neutralization by reaction with alkaline feedstocks (house et al., 2007; Rau et al., 2013; Sharifian et al., 2022). Potential alkaline feedstocks could be abundant natural silicate rocks such as basalts or olivine, or industrial byproducts of steel, aluminum, and cement manufacturing. (Campbell et al., 2022; Renforth, 2019). In each of these cases, the decrease in calcium ion concentrations can be overwhelmed by the larger shift in carbonate equilibrium toward HCO₃⁻ and
CO$_2$ such that $\Omega_{\text{avg}}$ would increase. Each of these approaches, however, reintroduces their implementation concerns that should be examined critically for their local and global impacts.

Process scalability should be demonstrated before the proposed process is considered a commercially viable solution. Coupling the MICP process with the existing desalination infrastructure offers various advantages for scale-up. Seawater desalination plants already have the capacity to pump and treat over 100 million m$^3$ of seawater and brackish water per day, which produces a roughly equivalent amount of concentrated seawater (>50 g/L) (Eke et al., 2020). Coupling BPMED and MICP with desalination plants also has economic benefits. The seawater effluent of desalination plants has a higher conductivity than natural seawater, due to its higher concentration in mobile ion charge carriers and can be used to reduce the energy consumption of electrodialysis devices (Sharifian et al., 2022; Tanaka et al., 2003; Yasukawa et al., 2020). The scale of ocean-based indirect carbon removal is often limited by its accessibility, i.e., the ability to integrate itself within the existing infrastructure. In a large-scale system, the cost associated with ocean water intake/discharge (i.e., pre-treatment, piping, and pumping) is expected to make up a significant portion of the total expenditure (Digdaya et al., 2020). A techno-economic analysis (TEA) on an indirect ocean capture plant (Eisaman et al., 2018) provides insights into how desalination plant coupling reduces capital and operating costs. It was estimated that incorporating desalination plants could reduce the total costs per ton of CO$_2$ extracted by 55% (Eisaman et al., 2018). Experimental work via lab/pilot scale demonstrations will be necessary to derive the inputs for an accurate life cycle assessment (LCA) and TEA, on the envisioned system. Furthermore, only when a resultant value-added material is characterized can a reference flow from the system be developed (Zimmermann et al., 2020). Subsequent studies will consider the technological capability, cost, and limitations (i.e., regional restrictions) of the envisioned system (Marecos et al., 2022; Zimmermann et al., 2020).

Photobioreactors, which are specifically designed for culturing phototrophic organisms, need to be scaled up. Table 4 summarizes the characteristics of various photobioreactor configurations and their scale-up potential. Designing an efficient photobioreactor is critical for the overall CO$_2$ removal performance according to the LCA. To effectively sequester large quantities of CO$_2$, a photobioreactor must have a high surface-to-volume ratio, mixing mechanisms, efficient mass transfer, and sufficient light exposure to facilitate photosynthesis (Kumar et al., 2011). Various photobioreactors have been developed for biological sequestration of CO$_2$ (e.g., continuous flat panels, airlift reactors, tubular reactors, etc.) with varying levels of success in scale-up demonstrations (Kumar et al., 2011). More recent developments involved hybrid reactor systems (Depra´ et al., 2020; Fu et al., 2021; Senatore et al., 2021).

As BPMED devices are still in their nascent stages of technology readiness, they are currently limited to lab-scale operation. However, there is considerable research on improving the membrane operational

### Table 3. Calculation approaches indicated as the master variables used to calculate the stream seawater chemistry at equilibrium, and the reasoning and assumptions behind these choices

| Calculation factors | Reasoning |
|---------------------|-----------|
| 1 DIC, Alkalinity   | Input DIC and Alkalinity are used to characterize the input seawater chemistry |
| 2 DIC, pH           | Target acid stream pH used. DIC degassing is assumed to be constrained, thus held constant. |
| 3 DIC, pH           | Target basic pH used. DIC dissolution is assumed to be constrained, thus held constant. |
| 4 DIC, Alkalinity   | DIC consumption by cyanobacteria used to calculate output DIC. Nutrient consumption effects are not considered because of their high variability depending on local conditions and marine cyanobacteria’s low nutrient requirements. |
| 5 DIC, Alkalinity   | Changes in DIC and Alkalinity due to carbonate precipitation and subsequent linear mixing of the acidified and basified streams are used to calculate effluent’s DIC and alkalinity. |
### Table 4. Photoreactors and optimal conditions for scaled-up CO₂ sequestration using cyanobacteria

| Reactor type       | Characteristics                                                                 | Conditions for Optimal Photosynthesis                                                                 | Risks and Challenges to CO₂ sequestration                                                                 | Suitability for Scale-Up | References                                                                 |
|--------------------|---------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------|--------------------------|--------------------------------------------------------------------------|
| Air lift           | Two compartments (internal and external loops): one contains gas (riser) and other does not (downcomer) | Large-scale cultivation of microorganisms (good light use, temperature control, high mass transfer coefficient) | Difficult to scale-up due to gas residence in various compartments (impact turbulence, mixing, gas-liquid mass transfer, heat transfer); low hydrodynamics stress on microorganisms | No                       | (Bahadar and Khan, 2013; Bai et al., 2011; Janssen et al., 2003; Kumar et al., 2011) |
| Bubble column      | Tall cylindrical vessel; affordable to purchase and maintain                     | Requires external light, works best in shorter light and dark cycle                                      | No mixing mechanics; no agitation; sparged gas moves upward; mixing/stirring required for CO₂ sequestration | Yes                      | (Bahadar and Khan, 2013; Kuhne et al., 2014; Kumar et al., 2011; Nagase et al., 1998; Wijanarko et al., 2004) |
| Flat panel         | Flat, cuboid with a short light path; often made from transparent panels         | Light often externally supplied; adjustable light path to achieve higher/lower light saturation levels  | High-stress damage related to aeration; a power supply of 53 W/m³ needed to induce mass transfer rate high enough to avoid O₂ gas accumulation which may damage microorganisms | Yes                      | (Bahadar and Khan, 2013; Degen et al., 2001; Kumar et al., 2011; Sierra et al., 2008) |
| Helical tubular    | Transparent, coiled, flexible tube of small diameter; centrifugal pump drives culture through a long tube to the degassing unit; degassing unit can be independent or attached | Cone shape provides high light-harvesting efficiency without changing basal area                        | Limited scalability—the centrifugal pump needs high amount of energy, high heating, and lighting costs; high shear stress; problems with fouling | No                       | (Bahadar and Khan, 2013; Kumar et al., 2011)                                |
| Horizontal or vertical tubular | Tubes arranged horizontally or vertically in parallel positions to maximize light exposure | Suitable for outdoor cultivation (high biomass yields, short harvest times); efficient temperature control and lighting; high surface area enhances light energy input efficiency | CO₂ in the exhaust gas is likely to be released to the atmosphere than sequestered; cell growth and fouling in corners or along walls; slow mass transfer of CO₂ into liquid medium (low growth rate of microorganisms) | Depends on reactor setup | (Bahadar and Khan, 2013; Kumar et al., 2011; Pires et al., 2017; Qin and Wu, 2019; Ugwu et al., 2003; Yang et al., 2016) |
| Stirred tank       | Vessel with stirring system and relatively large volume (1–3 L), sometimes with blade agitators; temperature control usually available, no light | High growth rate of cyanobacteria—CO₂ bubbled at the bottom of reactor provide growing bacteria carbon source, external light supply needed | Limited scalability due to the low surface area, high shear stress | No                       | (Bahadar and Khan, 2013; Kumar et al., 2011; Sydney et al., 2019)          |
durability, translating to decreased operating costs via prevention and reduction in membrane maintenance (Blommaert et al., 2021). The advantage of using BPMEDs resides in a multi-stack configuration (Digdaya et al., 2020). In this case, the contribution of applied electrode potential to the total applied potential scales inversely with stack size, meaning that a multi-stack configuration reduces the total electrochemical energy consumption (Eisaman et al., 2012). However, in a scaled-up system, ions move across larger distances and encounter more ohmic resistance losses as they migrate across individual layers and chambers. As a result, one can consider the trade-off between the stack size and electrode area to achieve efficient BPMED systems and desirable throughput (Blommaert et al., 2021; Digdaya et al., 2020). Additionally, to reduce electrochemical energy consumption and pumping costs, it may be technologically and economically more viable to utilize BPMED to generate smaller volumes of highly acidic and basic streams of seawater that are diluted to the desirable seawater streams. This dilution process removes the requirement of a BPMED system for handling large volumes of seawater.

COMPARISON AMONG OCEAN CARBON REMOVAL STRATEGIES

In the context of the oceanic carbonate system, total alkalinity (TA) is a measure of the amount of proton acceptors (bases) in excess relative to proton donors (acids) (Wolf-Gladrow et al., 2007). Proton acceptors and donors are defined relative to the molecular CO$_2$ when donating zero protons (Equation 8). For example, HCO$_3^-$ and CO$_3^{2-}$ can accept 1 and 2 protons, respectively, and thus, respectively, have a proton level of −1 and −2 concerning molecular CO$_2$ (Wolf-Gladrow et al., 2007).

\[
TA = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] + \text{minor constituents} \quad \text{ (Equation 8)}
\]

Bicarbonate and carbonate ions collectively contribute around 96% of total alkalinity in seawater (Zeebe, 2001). The CO$_2$ removal effects under various ocean CDR strategies can be compared by the outcomes of TA and DIC changes. While TA can be experimentally determined, it is not immediately obvious how it changes as a result of prospective ocean CDR strategies due to the non-conservative nature of their complex constituents. A conservative quantity here is one that remains constant with changes in pH, temperature, and pressure (Zeebe, 2001). By applying a charge-neutrality condition, an explicitly conservative TA, which defines alkalinity as the difference in its conservative cations and anions can be derived (Equation 9) (Wolf-Gladrow et al., 2007). This is more applicable for the measurement and comparison of largely different ocean CDR strategies (Wolf-Gladrow et al., 2007).

\[
TA_{EC} = \sum \text{conservative cations} - \sum \text{conservative anions} + \text{minor constituents} \quad \text{ (Equation 9)}
\]

Electrochemical ocean CDR strategies, which vacuum strip CO$_2$ from an acidified stream, remove DIC but do not affect alkalinity as long as the acid and basic streams merge later on. The effluent stream may have a higher pH, but the TA remains constant. As no conservative cations or anions are consumed or produced in the process, the explicitly conservative expression for TA makes it clear that alkalinity is constant.

Ocean liming and enhanced weathering are two examples of ocean alkalinity enhancement (OAE) strategies whereby ocean alkalinity is increased by the addition of lime, CaO (Equation 10) or the dissolution of carbonates or silicate minerals (Equations 11 and 12) (Renforth, 2019; Renforth et al., 2013).

\[
\text{CaO(s) + 2CO}_2{\text{(aq)}} + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+}{\text{(aq)}} + 2\text{HCO}_3^- \quad \text{ (Equation 10)}
\]

\[
\text{CaCO}_3{\text{(s) + CO}_2{\text{(aq)}} + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+}{\text{(aq)}} + 2\text{HCO}_3^-} \quad \text{ (Equation 11)}
\]

\[
\text{CaSiO}_3{\text{(s) + 2CO}_2{\text{(aq)}} \rightarrow \text{Ca}^{2+}{\text{(aq)}} + 2\text{HCO}_3^-{\text{(aq)}} + \text{SiO}_2{\text{(aq)}}} \quad \text{ (Equation 12)}
\]

Ocean liming, silicate weathering, and carbonate weathering all add 2 mol of alkalinity per 1 mol of added minerals. Carbonate weathering also adds 1 mol of DIC by introducing CO$_3^{2-}$. As a result, ocean liming and silicate weathering sequester almost twice the amount of atmospheric CO$_2$ as carbonate weathering does (Renforth, 2019). Our comparison of similar strategies shows the relevance of the proportional changes in DIC and TA for a given ocean CDR strategy. The above equations for enhanced weathering are far from exhaustive as various alkaline minerals have been proposed for OAE (Renforth, 2019). CaCO$_3$ precipitation (Equation 13) consumes twice as much alkalinity as DIC, thus is known to degas CO$_2$ in the ocean (Renforth, 2019; Wolf-Gladrow et al., 2007).

\[
\text{Ca}^{2+}{\text{(aq)}} + 2\text{HCO}_3^-{\text{(aq)}} \rightarrow \text{CaCO}_3{\text{(s)} + \text{CO}_2{\text{(g)}} + \text{H}_2\text{O(l)}} \quad \text{ (Equation 13)}
\]
Photosynthesis, e.g., by cyanobacteria can fix dissolved inorganic carbon by either dissolved CO$_2$ or HCO$_3^-$ ion uptake. These microorganisms maintain internal electroneutrality through ion transport systems (Wolf-Gladrow et al., 2007). In this case, HCO$_3^-$ uptake is facilitated by an Na$^+$/HCO$_3^-$ symport, where Na$^+$ is soon exchanged with H$^+$ via a Na$^+$/H$^+$ symport, such that total alkalinity is conserved (Mangan et al., 2016). If the process of organic carbon production, which is a sink of atmospheric CO$_2$, is coupled with microbial calcification, the combined effect can serve as a net CO$_2$ sink (Kamennaya et al., 2012; Suzuki, 1998). This is because, in addition to the inorganic carbon sequestered as CaCO$_3$, organic carbon is also sequestered within the biocement, meaning that the microbial DIC removal can overwhelm the CDR losses which stem from alkalinity consumption.

As MICP combines photosynthesis and CaCO$_3$ precipitation, its carbon negativity can be calculated based on the proportionality of their respective rates and effects on DIC and alkalinity. To simplify this calculation, 1 mol of DIC removal is assumed to correspond to 1 mol of atmospheric CO$_2$ removal. At small scales of removal, the influx of atmospheric CO$_2$ into the ocean can be expected to replace the DIC removed. 1 mole of alkalinity enhancement is assumed to correspond to 0.81 mol of atmospheric CO$_2$ removal, which is the average uptake efficiency of alkalinity addition across the ocean due to pH buffering (Tyka et al., 2022). This uptake efficiency is assumed to be symmetric, implying that 1 mol of carbonate precipitation corresponds to a $\sim$1.62 mol decrease in atmospheric CO$_2$ removal. 38.2 m$^3$ of seawater are required per kg of atmospheric CO$_2$ removed. If the flowrate of the stream 1 in Table 2 is scaled to remove 1000 tons of atmospheric CO$_2$ per year and extract over 86% of DIC, several photobioreactors with a total reactor volume of 987 m$^3$ are needed. Our findings under these assumptions are summarized in Table 3. The CO$_2$ is removed and sequestered in the form of a value-added, permanent product, i.e., biocement. In contrast, CO$_2$ extracted by membrane contactors and vacuum pumps needs to be further transformed or mineralized, incurring additional energy costs and carbon intensity. Furthermore, in the case of alkalinity regeneration (e.g., HCl extraction from the acid stream), the amount of seawater required per kg of CO$_2$ can be reduced to 12.8 m$^3$ seawater and the total photobioreactor volume required for the capacity to capture 1000 tons of CO$_2$ per year would be reduced to 382 m$^3$.

CONCLUSION AND OUTLOOK

Unlike previous pH-swing methods that rely solely on the acidified or basified ocean water for carbon removal, our proposed system utilizes both acidic and alkaline CO$_2$ capture. While there have been significant research efforts in the use of photosynthetic cyanobacteria and electrochemically mediated carbonate precipitation for carbon removal, our process combines naturally occurring carbon fixation of the former and efficacy and permanence of the latter respectively. This is achieved through enhanced microbial calcification facilitated by the efficient use of natural resources (i.e., sunlight and nutrients).

The use of naturally-occurring organisms leads to unique advantages. For acidic capture, where membrane contactors are typically used for degassing and stripping CO$_2$, cyanobacteria consume concentrated CO$_2$ spontaneously without the need for degas pre-treatment or electrical input. Bipolar membranes have demonstrated the ability to generate alkalinity at a fraction of the cost. Operating costs can be further offset via its end product, i.e., carbonate-encapsulated cyanobacteria bio cement. Such value-added products can be potentially developed and commercialized as self-healing concrete (Achal and Mukherjee, 2015; De Muynck et al., 2008; Ramachandran et al., 2001): Microbially induced calcium carbonate precipitation has been demonstrated to improve the strength and durability of cementitious materials, concrete self-repair, and crack sealing. Cement production accounts for 5%–7% of global anthropogenic emissions while increasing by 2%–4% yearly (van Ruijven et al., 2016; Zhang et al., 2018). Therefore, the production of carbon-negative cement alternatives opens up a pathway to reduce anthropogenic CO$_2$ emissions.

LIMITATIONS OF THE STUDY

This paper intends to provide insight into the feasibility of a hybrid electrochemical-microbial approach for ocean-based indirect CO$_2$ capture. The optimal process parameters needed for cyanobacteria growth, process scale-up, and economic analysis remain to be obtained. Testing the proposed system would require support from an interdisciplinary and global community. For example, the impacts of this system on the local ecosystem and global carbon and alkalinity cycle require a quantitative and systematic investigation.
LEAD CONTACT

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AUTHOR CONTRIBUTIONS

S.H. and N.B. conceived the idea. A.K., M.L., and R.Y. performed calculations. D.S. and M.I. collected and organized relevant literature. A.K., M.L., R.Y., M.I., and N.R. drafted figures and tables. D.S. and A.K. wrote the original draft. P.A., S.H., and N.B. supervised the project. S.H. and N.B. acquired the funding support. All authors revised and approved the final version of the manuscript.

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