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Ocean-Based Carbon Dioxide Removal

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Abstract

The global environment has been experiencing deleterious environmental effects, largely due to increased atmospheric CO_2 concentrations. This paper analyzes two *in-situ* electrochemical CDR methods, water electrolysis and bipolar membrane electrolysis (BPMED), that lower atmospheric CO_2 emissions by removing carbon from seawater. Both methods are conceptually viable and have distinct strengths and weaknesses.

Both gaseous CO_2 and solid $CaCO_3$ can be produced from these processes, but the team recommends an alkaline working pH to produce the latter. Processes with $CaCO_3$ production feature lowered capital and operating costs, more straightforward handling and storage methods, and increased downstream marketability. The team also recommends co-locating these marine CDR plant with a desalination plant to avoid the massive costs of pumping, pretreating, and piping large volumes of seawater.

The team estimated that for commercial-scale processes removing 1 Mt of CO_2 from desalination brine annually, an sCS^2 water electrolysis process will cost \$645 - \$664 per tonne of $CaCO_3$ while a BPMED process will cost \$405 - \$575 per tonne $CaCO_3$. With an assumed selling price of \$336 - \$370 per tonne $CaCO_3$, neither of these technologies are considered to be economically viable. Additionally, there are high levels of uncertainty surrounding their environmental effects at commercial-scale.

Because these *in-situ* electrochemical CDR methods likely will not be commercially-viable for several decades, the team estimates that they can be largely powered through renewable energy sources, promoting a circular economy and producing net-negative carbon emissions. Due to their shortcomings, the team suggests that these technologies be employed once the bulk of the CO_2 emissions have been removed; at this time, they alone cannot achieve the 10 Gt goal posed by the Paris Agreement.

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1 Introduction

Across the world, greenhouse gas (GHG) emissions are steadily rising, reaching an all-time high of 36.3 billion tonnes (36.3 Gt) in 2021,[1] of which the United States and China, the two largest single-nation contributors, are responsible for 5.2 Gt and 10.7 Gt,[1] respectively. With these rising emissions, the global environment has endured painfully noticeable effects through historical highs in global temperatures[2] and ocean levels,[3] record lows in Antarctic and Greenland ice cap mass,[4] and abnormally extreme weather events becoming more routine.[6] The data for each of these statistics can be viewed in Figures 3 through 9 in Appendix B.1. While society attributes this devastating environmental fallout to GHGs as a whole, carbon dioxide makes up an overwhelming majority of these emissions, accounting for 79% in 2020,[6] illustrated in Figure 4 in Appendix B.1. In fact, the global CO_2 concentration reached 400 ppm in 2021[9] and is expected to continue to rise.

Many massive international legislative efforts, such as the Paris Agreement treaty[7] in 2015, have been adopted in an attempt to increase carbon dioxide removal (CDR) methods, while decreasing global reliance on fossil fuels. To reach the treaty's ambitious goal of limiting climate change to 1.5°C, it is estimated that around 10 Gt of carbon[7,8] must be removed annually by 2050. While this value is staggering, and likely unattainable with today's technologies, significant CDR efforts can be made through ocean-based techniques.

Both atmospheric and marine CDR pathways were considered for discussion in this paper, but it is believed that the latter has greater potential at scale,[8] due to improved CDR performance as well as superior economic viability. Furthermore, because carbon concentrations are closely coupled between the oceans and the atmosphere,[7,8] any reduction in atmospheric concentrations without complementary marine CDR will be futile as the oceans will release any recovered carbon back into the atmosphere to restore equilibrium.

Because the ultimate goal is to reduce atmospheric carbon levels, this inherent coupling suggests that oceans are a logical place to investigate CDR pathways. These marine CDR ventures are strongly supported by the sheer size of the oceans, as well as their massive role in the global carbon cycle. In fact, it is estimated that the oceans have absorbed approximately 25 - 40% of anthropogenic carbon emissions since the Industrial Revolution.[7,15] Additionally, CO_2 is approximately 150x more concentrated in the ocean than it is in the atmosphere per unit volume,[16,25] meaning that marine CDR methods require a significantly smaller volume of feedstock. This, in turn, leads to higher efficiencies and reduced carbon footprints.[15,23] The Energy Futures Initiative[7] estimates that marine CDR facilities require as little as one-tenth of the area needed for comparable land CDR facilities.

This paper investigates two *in-situ* electrochemical CDR pathways, water electrolysis and bipolar membrane electrodialysis (BPMED), that utilize a "pH-swing" concept to capture carbon from seawater.[8] This will be explained in more detail in Section 2, where the team completes a comprehensive literature review and demonstrates proof-of-concept for each pH-swing electrochemical technology at lab-scale. From these pathways, the team separated these technologies into two pathways on whether they produce gaseous CO_2 or solid $CaCO_3$, which have dissimilar downstream processes and value chain opportunities. Additionally, the team briefly discusses coupling these CDR plants with desalination and artificial upwelling/downwelling[7] that may be viewed as useful complements at commercial-scale. The details for these methods are shown in Section 3.2.

The team's goal with this project is to effectively scale up negative-emission CDR technologies in order to remove 1 million tonnes (1 Mt) of dissolved carbon from the oceans annually. While an initial goal of 1 Mt is a fraction of a percent[1] of the total global emissions, the team believes it to be a reliable baseline to demonstrate technological viability at scale. An economic evaluation, and a potential value chain for these CDR techniques at commercial-scale, will be analyzed in Section 3. Section 4 analyzes potential adverse environmental effects of these CDR facilities. The team concludes their findings and provides final recommendations in Section 5, followed by a brief examination of the future plans for this project in Section 6.

2 Marine CDR at Lab-Scale

It is well-documented that the oceans have dissolved inorganic carbon (DIC) levels around 2.3 mM, of which 95% is in the form of aqueous carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions and can be accessed fairly easily.[8,19] In this section, the team proposes two *in-situ* electrochemical CDR methods, water electrolysis and BPMED,[8] that have shown the ability to effectively lower DIC concentrations in seawater by producing either gaseous carbon dioxide (CO_2) or solid calcium carbonate ($CaCO_3$).

These electrochemical methods are advantageous over direct air capture (DAC) because it enables carbon recovery from ocean water at ambient temperatures and pressures without requiring additional chemicals.[8,19,23] Additionally, DAC processes utilize a large variety of liquids or high surface area solids to act as sorbents, while for marine CDR, oceanwater acts as a natural sorbent and effectively decreases its overall costs.[8,23]

Electrochemical techniques also have the added benefit of being relatively energy efficient because they can target the carbon molecules directly instead of the surrounding medium.[8] Despite these improvements, however, these electrochemical CDR methods still have fairly large energy requirements. Because many of these technologies are decades away from commercial-scale viability, it is assumed that they can be powered largely through renewable energy sources for net-negative carbon emissions.[14,23]

As mentioned in Section 1, the team focuses primarily on two *in-situ* electrochemical CDR technologies that utilize the concept of "pH-swing" to recover carbon from seawater. It is worth noting that several other electrochemical CDR methods exist that do not utilize this pH-swing technique, such as molten-carbonate cells or redox-active carriers,[7,8] but are outside the scope of this paper and will not be discussed. The pH-swing technique functions by continuously varying the pH of the solution over wide ranges to manipulate the thermodynamic equilibrium of CO_2 in solution, allowing for fairly straightforward absorption and desorption at ambient temperatures and pressures.[8,16]

Below are the chemical kinetics for these processes, largely simplified for brevity.[8,16] Equations 1 and 2 show the effects of the water dissociation reaction on the CO_2/HCO_3^- equilibrium in seawater and is applicable for both acidic and basic pathways. Equation 3 demonstrates the thermodynamic equilibrium for the acidic-pH process that produces gaseous CO_2,[8] while Equations 4 and 5 show the thermodynamic equilibrium for the alkaline-pH process that produces solid $CaCO_3$.[16]

$$H_2O \rightleftharpoons OH^- + H^+ \tag{1}$$

$$CO_2\ (aq) + OH^- \rightleftharpoons HCO_3^- \tag{2}$$

$$CO_2\ (aq) \rightleftharpoons CO_2\ (g) \tag{3}$$

$$HCO_3^- + OH^- \rightleftharpoons H_2O + CO_3^{2-} \tag{4}$$

$$CO_3^{2-} + Ca^{2+} \rightleftharpoons CaCO_3 \tag{5}$$

According to Equation 2, when the solution is acidified, the OH^- concentration is lowered, converting the HCO_3^- into dissolved CO_2 where it can be separated fairly easily. This phenomenon essentially forms the backbone of these CDR processes and places a heavy emphasis on returning alkalized seawater back into the oceans, where it reabsorbs CO_2 from the atmosphere.[8,16] As the concentration of CO_2 increases in solution, the concentration of CO_2 in air also increases in turn due to Henry's Law, shown in Equation 3.

This gaseous CO_2 is considered to be the "end-product" for these acidic-pH processes and when it is captured, it is effectively removed from the system, creating a positive feedback loop that promotes the production of additional gaseous CO_2.[8] By continuously shifting the working pH between acidic and basic levels, the system is able to continuously absorb and release carbon from seawater in an advantageous way.

This process is similar for alkaline-pH levels, as the first two equations mirror those for the acidic-pH process. However, the OH^- concentrations are now increased. As the concentration of OH^- increases, it promotes the production of HCO_3^-, shown in Equation

5, and eventually CO_3^{2-}, shown in Equation 6. These CO_3^{2-} ions combine with excess Ca^{2+} ions, as shown in Equation 7, to form $CaCO_3$, which is precipitated out of solution.[16] As with gaseous CO_2 production, once the "end-product" $CaCO_3$ precipitates from solution, it is effectively removed from the system, which promotes further $CaCO_3$ production as equilibrium is restored.[16] Because Ca^{2+} ions are present in excess of DIC in seawater,[17] this mineralization method, in theory, is capable of removing all DIC from seawater.

2.1 Water Electrolysis

The first *in-situ* electrochemical technique the team suggests to capture carbon from seawater is water electrolysis, which enables pH-swing in the vicinity of two electrodes. Using an ion-exchange membrane, alkali absorbent (seawater) regeneration is possible, and co-production of hydrogen gas can reduce the overall cost of the process by being a source of negative-emissions fuel. To avoid undesired secondary reactions and to mitigate electrode contamination, water electrolysis units usually utilize two ion-exchange membranes (IEM) that are inserted between the cathode and anode. The following sections detail two lab-scale water electrolysis experiments that were capable of capturing carbon from natural seawater, generating gaseous CO_2 or solid $CaCO_3$ as the final product.

2.1.1 Water Electrolysis Producing Gaseous CO_2

For gaseous CO_2 production from seawater via water electrolysis, the team investigated research done by the United States Naval Research Laboratory in Key West, Florida.[23] These researchers designed an electrolytic cation-exchange module (E-CEM), depicted in Figure 1 below, that continuously pumps seawater at a rate of 1900 mL/min.

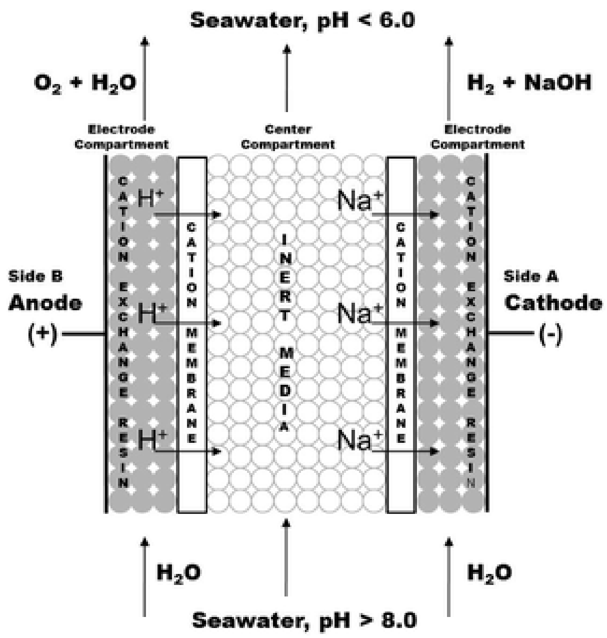

Figure 1: Water Electrolysis Schematic for CO_2 Capture & H_2 Production

The oceanwater enters the module through the center chamber, where the aqueous HCO_3^- and CO_3^{2-} ions are converted into carbonic acid, or H_2CO_3. When direct current is applied to the cell, it produces H^+ ions, O_2 gas, and spare electrons at the anode, creating an acidified seawater effluent.[23] This is done through the migration of H^+ from the surface of the anode, across a cation-permeable membrane, and into the center holding compartment, where it reacts with the flowing seawater. The CO_2 gas is then vacuum stripped via specialized membrane contactors, resulting in a highly purified CO_2 stream with trace amounts of water vapor and air.[23]

Meanwhile, the cathode side is producing OH^- ions, H_2 gas, and an alkaline NaOH solution. This basic solution is recombined with the acidified effluent stream, restoring the solution to its original pH. While it is common for water electrolysis units to dispose of extraneous H^+ ions with the waste from the anode, this process utilizes these ions in the central compartment to acidify the seawater, maintaining a pH around 6.[23]

To prevent calcium and magnesium precipitate buildup on the electrodes, the researchers regenerated the electrodes at regular intervals via polarity switching, also known as polarity cycles.[23] This regeneration is crucial to the performance of the cell, mitigating significant module degradation at high pH levels. Using two consecutive polarity cycles at an applied current of 20 A, the research team removed 92% of the CO_2 in the effluent seawater. Furthermore, they determined a maximum H_2 production rate of 222 mL/min with a total energy consumption of 49 kWh/m^3 H_2 or 179.6 kJ/mol CO_2 at STP.[23]

2.1.2 Water Electrolysis Producing Solid $CaCO_3$

For carbonate production from seawater, the team investigated a single-step carbon sequestration and storage (sCS^2) process designed by UCLA's Institute for Carbon Management. This process, pictured in Figure 10 in Appendix B.2, is designed to precipitate $CaCO_3$, $MgCO_3$, and various hydroxy-carbonates.[25]

These precipitations are achieved by reacting aqueous CO_2 with Ca^{2+} and Mg^{2+} ions in seawater using electrolytic flow reactors at an alkaline pH.[25] The precipitates are filtered out of the solution through sedimentation and dried with belt presses before being discharged back to the ocean or stored. The research team from UCLA determined that because this sCS^2 process uses Ca^{2+} and Mg^{2+} ions already dissolved in seawater, it is not limited by the availability or reactivity of the seawater feedstock.[25] Additionally, they acknowledged that because the sCS^2 process does not require membranes, it is not affected by membrane fouling, and therefore provides an efficient CDR process that can be easily scaled-up.[25]

As said in Section 2, discharging the alkalized seawater back into the ocean promotes reabsorption of atmospheric CO_2, resulting in a net-negative emissions process. In fact, the researchers noted that this process allows for further reabsorption of CO_2 from the atmosphere via the discharge of realkalized anolyte.[25] The researchers determined the overall energy consumption for this process to be between 0.07 - 2.3 kWh/tonne CO_2, which does not include energy requirements for water intake or pretreatment.[25] They also noted that the H_2 gas was produced with an overall process efficiency of 90%.

2.2 Bipolar Membrane Electrodialysis (BPMED)

The second *in-situ* electrochemical method the team suggests to capture carbon from oceanwater is bipolar membrane electrodialysis (BPMED). Bipolar membranes (BPMs) are a subset of ion-exchange membranes that are created by laminating a positively-charged anion-exchange layer (AEL) and a negatively-charged cation-exchange layer (CEL) together.[8,18] BPMs are typically made up of a polymer matrix, various functional groups, and a supporting matrix that increases the overall mechanical strength.[18] CEL functional groups are usually sulfonic acid groups designed for cation-exchange, while AELs contain quaternary ammonium groups for anion-exchange.[18]

In the presence of an electric field, BPMs are capable of dissociating water to generate H^+ and OH^- ions, affecting the pH of the solution.[8] These membranes are designed such that H^+ ions leave through the CEL and the OH^- ions leave through the AEL, which produces an acid and a base on opposite sides of the membrane and gives a pH gradient.[18] Because many BPMED cells incorporate a three-compartment design, as demonstrated in Figure 2 below, the ocean salt is separated from the acid and base streams, allowing production of acids and bases with relatively high purities.[18]

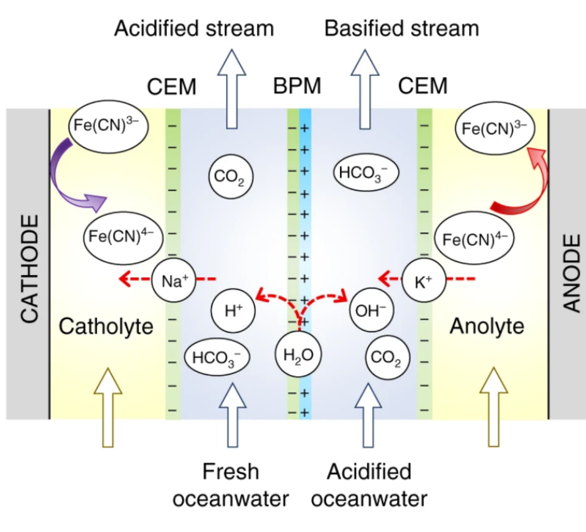

Figure 2: BPMED Cell Schematic for CO_2 Capture

By controlling this electric field and the resulting ion concentrations, one can effectively manipulate the pH of the solution over a wide range. In the following sections, the team investigates several lab-scale BPMED experiments that successfully demonstrated the ability to remove carbon from natural seawater, generating either gaseous CO_2 or solid $CaCO_3$.

2.2.1 BPMED Producing Gaseous CO_2

For CO_2 production from seawater, the team investigated lab-scale BPMED experiments that were conducted by researchers from Delft University of Technology[16] and California Institute of Technology.[15] Using a setup similar to that described in Figure 2, both research teams discovered that gaseous CO_2 can be captured from seawater at an acidic pH with the inclusions of specialized membrane contactors for vacuum stripping.[15,16] It was discovered that the CO_2 production rate increases linearly with the applied current density on the cell, but only to a certain point, as BPMED is considered to have an optimal operating range to maximize overall efficiencies.[15,16]

The team from Delft University of Technology discovered that BPMs cannot operate properly at extremely low current densities because it may result in ion leakage through the membrane, lower productivity and dissociation rates, and product contamination.[16] Likewise, they found that the BPM will not operate properly at extremely high current densities, as it reduces the BPM's permselectivity, leading to Faradaic inefficiencies and large energy consumption requirements without noticeable increases in production rates.[16]

The researchers from Delft University of Technology determined the optimal current density to be 10 - 20 mA/cm^2 and estimated the overall energy consumption to be around 1.58 - 2.53 kWh/kg CO_2.[16] Meanwhile, the team from the California Institute of Technology found an optimal current density between 1.5 - 3.5 mA/cm^2 for their setup with a reduced overall energy consumption of 0.98 kWh/kg CO_2, which was achieved by eliminating voltage losses at the electrodes.[15] This team also demonstrated that by using three membrane contactors in series, CO_2 could be removed at an overall capture efficiency of 70%.[15]

2.2.2 BPMED Producing Solid $CaCO_3$

For $CaCO_3$ production from seawater at lab-scale, the team reviewed research conducted by researcher teams from Delft University of Technology[16] and Hebei University of Technology.[17] The procedure for each experiment was similar for those designed for CO_2 capture, but the working pH was instead set to an alkaline level.

The researchers from Delft University of Technology employed a semi-scaled BPMED setup with ten cell pairs and discovered that of the theoretical maximum 2.3 mM DIC in natural seawater, as stated in Section 1, a maximum of 2.078 mM (90%) is actually extractable.[16] As with their CO_2 experiment, the research team confirmed that $CaCO_3$ production increases linearly with applied current density and found that current densities over 20 mA/cm^2 can produce up to 208 mg $CaCO_3$ per liter of seawater, mainly in the form of aragonite.[16] In their experiment, they were capable of removing about 75% of DIC from seawater with an energy requirement of 0.88 kWh/kg $CaCO_3$, acknowledging that the energy requirement can be lowered to a theoretical minimum of 0.097 kWh/kg $CaCO_3$.[16]

The researchers also discovered that at basic pH levels, minor amounts of brucite ($Mg(OH)_2$) and slaked lime ($Ca(OH)_2$) coprecipitate, but found that between pH 9.6 and 10, these auxiliary hydroxide precipitation reactions were minimized.[16] It is worthwhile to note that these hydroxide precipitates are nontoxic, but at large enough concentrations, may need to be filtered out of the final product before it can be considered marketable.

Meanwhile, the team from Hebei University of Technology utilized a specialized four-chamber BPMED unit that produced carbonate ions in an alkaline chamber and combined them with seawater in a separate salt chamber to prevent membrane fouling.[17] Downstream, this mixture is channeled into a seeded crystallizer to produce solid $CaCO_3$, mainly in the form of calcite. They also found minor amounts of brucite precipitate, but considered it to be in negligible concentrations in the final product.[17] Their experiment showed an overall capture efficiency around 73% with an energy requirement of 6.46 kWh/kg $CaCO_3$, but is estimated that it can be lowered to around 3 kWh/kg $CaCO_3$.[17] A process flow diagram detailing each research team's experimental setup with design parameters can be viewed in Figures 11 and 12 in Appendix B.2.

2.3 Water Electrolysis Versus BPMED

2.3.1 Water Electrolysis Pros & Cons

The main upside for water electrolysis is the co-production of H_2 gas at the cathode during the production of gaseous CO_2 and solid $CaCO_3$. This H_2 gas can be utilized downstream for thermal catalytic processes to make hydrocarbons from CO_2, acting as a green fuel.[23,25] Alternately, the H_2 gas can be re-electrified and recycled to provide power for the electrochemical cell. Additionally, although there is a significant cost incurred, using ion-exchange membranes for bicarbonate and gaseous CO_2 production prevents the production of Cl_2 gas and electrode contamination, which are serious risks during marine-based operation.[24] Alternately, researchers at UCLA studying sCS^2 suggest using oxygen evolution reaction (OER)-selective coatings in the anode to mitigate Cl_2 gas production.[25]

Producing carbonates through water electrolysis can be a cost-effective method to generate hydroxide solutions, benefiting from favorable thermodynamics.[24] For the sCS^2 process, generating the alkaline solution locally with the flow-through electroactive mesh electrodes improves the kinetics of $CaCO_3$ precipitation. This is achieved through Joule heating at the mesh surface, causing increased pH and temperatures, promoting supersaturation.[25] Additionally, using the softened water produced by the sCS^2 process as feed for desalination plants can result in significantly reduced energy requirements, estimated to be around 9% lower than for stand-alone processes.[33] Finally, because the sCS^2 process does not require membranes, it is immune from membrane fouling, providing an optimized process that maximizes yield and facilitates upscaling.[23,25]

That being said, there are still several shortcomings with incorporating these technologies at scale. Primarily, in order to achieve the 1 Mt annual goal, it is estimated that trillions of dollars in capital expenses and energy costs are needed for the development of several large-scale CDR plants.[25] Another major downside to water electrolysis is that co-production of the green fuel H_2 gas introduces heightened energy requirements and costs involved in producing and storing the gas safely.[23]

While producing gaseous CO_2, water electrolysis also suffers from module degradation due to calcium and magnesium precipitation on the electrodes, so they need to be regenerated at regular intervals.[23] These concerns are mirrored in the bicarbonate production process, as there is potential for carbonate or hydroxide precipitation onto the cathode, which may negatively affect the performance of the electrolysis cell.[24] Also, potential biofouling of the membrane resin beads during the E-CEM water electrolysis process may pose a potential safety risk at large scales.[23]

2.3.2 BPMED Pros & Cons

BPMs have been gaining traction in materials science and chemical engineering applications in recent years over conventional acid/base production methods due to their technical, economic, and environmental optimizations.[18] One major area of improvement over other acid/base production methods is that the water dissociation reaction during BPMED occurs without gas evolution, such as H_2 or O_2 gas, which leads to lower overall energy requirements.[13,16] In fact, BPMED energy requirements are estimated to be 40-50% less than for comparable water electrolysis processes.[8,18]

However, there are still several downsides to current BPMED technology. For example, smaller pH swings come at the cost of significantly slower chemical kinetics with no potential for catalysis, as commercially-viable BPMED catalysts are still an active area of research and are decades away from implementation.[16,18] Another downside to BPMED, as with most membrane-based separations, is the potential for membrane fouling (also known as scaling). Fouling occurs when compounds precipitate onto the membrane, amplifying the pressure drop across the membrane and increasing the overall energy consumption of the cell. Membrane fouling also can cause non-uniform flow, which significantly decreases the membrane lifetime and production rates.[8,16,18]

Because membrane fouling is such a significant concern for BPMED processes, especially at scale, there have been several suggested remedies throughout literature. For example, researchers found that using a pure NaCl solution during the BPMED phase can prevent fouling once the generated NaOH is added to the seawater via a controlled crystallizer.[8,17] Another method involves periodically rinsing the membranes with HCl and water to prevent fouling from building up.[16] Most notably, researchers from Mountain View, California found that by coupling BPMED processes with an upstream desalination process, the potential for membrane fouling decreases significantly.[13,14] This analysis has several important notes for commercial-scale marine CDR and will be analyzed in greater detail in Section 3.

3 Marine CDR at Commercial-Scale

3.1 Downstream Applications for Recovered CO_2 & $CaCO_3$

As indicated in Section 1, the ultimate goal of this project is to effectively scale up these negative-emission CDR technologies in order to remove 1 Mt of carbon from the oceans annually. In order to adequately analyze the economic viability of this goal, and to rule out a few of the potential pathways, the team decided to first compare the downstream opportunities for recovered gaseous CO_2 against those for solid $CaCO_3$.

3.1.1 Industrial Uses for Recovered CO_2

As of today, carbon capture and storage (CCS) technology represents one of the most widely used downstream pathways for recovered CO_2, and is widely believed to be the most viable industrial-scale storage method.[10] According to CCS technology, once the carbon has been recovered, it is injected into underground geological formations, such as saline aquifers or oil and gas reservoirs, and stored there indefinitely. Once it has been sealed inside these formations, the gas will need to be constantly monitored for corrosion and leakage back into the atmosphere, often with timescales in the thousands of years.[7,19]

Because there is limited economic benefit from these CCS technologies, and because there is a large degree of uncertainty during its lifetime,[19] the team rejected CCS technologies from consideration and removed them from the potential value chain. Instead, the team found it to be more feasible to convert the recovered carbon into long-lived, industrially-marketable products through carbon capture and utilization (CCU) pathways.[10]

There are many industries today that utilize CO_2 as a raw material, such as fertilization, oil/gas recovery, food/beverage production, metal fabrication, refrigeration, fire suppression, and specialty chemical production.[10] With an estimated global market value between $6B - $11B in 2020, approximately 230 Mt of CO_2 were used as a raw material around the world, with the fertilizer and oil/gas industries leading the demand.[8,10] This corresponds to an average selling price of $26 - $48 per tonne CO_2.

Despite the wide variety of industrial applications, the team prioritized industries that produced long-lived carbon products to prevent companies from re-emitting the captured carbon back into the atmosphere. For example, the oil/gas industry's enhanced oil recovery process has one of the world's largest demands of externally-sourced CO_2, but it promotes accelerated carbon emissions without a sufficient carbon mitigation process.[10]

3.1.2 Industrial Uses for Recovered $CaCO_3$ and $MgCO_3$

As with CO_2, $CaCO_3$ has a large variety of industrial uses, such as cement and construction materials, paper filler, paints and powder coatings, plastic/rubber manufacturing, and adhesive production.[19] The global market for $CaCO_3$ was estimated to be between $39B - $43B in 2020 with an aggregate demand of 116 Mt,[16] of which the paper and cement/construction industries were the two largest consumers. This corresponds to an average selling price of \$336 - \$370 per tonne $CaCO_3$.

$MgCO_3$ also can be utilized in a large variety of industries, such as refractory brick production, flooring, fireproofing, cosmetics, toothpastes, and medicines,[34,35] with a global market valued around \$250M.[34,35] Because this market is considerably smaller than that for $CaCO_3$, and because $MgCO_3$ is produced in such small quantities during these marine CDR processes, the team decided to reject it from potential value chains.

The main advantage of converting recovered carbon into solid $CaCO_3$ instead of gaseous CO_2 is that it demonstrates a safer and more permanent storage method with no risk of leakage back into the atmosphere.[16,19] $CaCO_3$ also requires little to no purification before it can be considered marketable, whereas CO_2 requires various purity levels depending on its downstream industrial utilization.[10] Additionally, $CaCO_3$ production eliminates the need for membrane contactors, which provides considerable capital expenditure savings.[13,14]

Because of the cost efficiencies,[13,14] the more straightforward handling and storage methods, and the larger global market,[10] the team decided to move forward with $CaCO_3$ as the main product for these marine CDR processes. The following sections analyze the economic viability of commercial-scale water electrolysis and BPMED processes that remove 1 Mt of CO_2 from desalination brine annually, followed by the proposal of a potential value chain.

3.2 Advantages of a Co-Located CDR Plant

As mentioned in Section 2.3.2, there are numerous benefits to co-locating marine CDR plants with upstream desalination plants. With a theoretical maximum of 2.078 mM DIC in natural seawater (see Section 2.2.2), trillions of liters of seawater are needed in order to achieve the annual 1 Mt goal. By coupling these CDR processes with desalination plants, all the seawater pumping, pretreating, and piping costs are assumed by the desalination plant, drastically reducing the capital and operating costs for the CDR process.[13,14] This partnership is massively beneficial, as a co-located plant has overall costs that are approximately 60% lower than a stand-alone CDR plant.[13,14]

Furthermore, it was determined that by using the reject brine stream from the desalination plant as the input to these CDR processes, the overall CDR process efficiency increases between 200% - 300%. This is due to increased DIC levels in the brine, which reaches 6 mM,[13,14] increasing the amount of carbon per unit volume and decreasing the overall volume of seawater required.

Recent studies suggest that this coupling can be mutually beneficial as well, demonstrating that the alkalized seawater output from the CDR plant can help preserve the desalination plant's reverse osmosis membranes. However, this alkalized seawater cannot be directly returned to the desalination plant because it needs time to reabsorb atmospheric CO_2. It is estimated this process takes about a year to complete,[13] but the Energy Futures Initiative suggests that this timetable can be expedited with the introduction of artificial upwelling/downwelling in the oceans.[7]

Upwelling/downwelling, analogous to soil tilling for agricultural applications, involves mixing the oceans to allow nutrient-rich water to rise to the ocean surface.[7] This water can increase the rate and selectivity of the electrochemical processes, which in turn can increase the overall throughput and purity values of the recovered product.[7] Although the adjusted timeline for this reabsorption process is assumed to be less than one year, an exact schedule is unclear as it depends on mixing rates, ocean currents, and weather patterns, representing an area of active research.

Despite these benefits, this partnership may be difficult to accomplish at commercial-scale. The largest desalination plant in the world, Ras Al-Khair in Saudi Arabia, currently produces 1.04 billion liters (6.54 million barrels) of brine daily,[11,12] which is a fraction of the required input for a marine CDR plant with a 1 Mt annual target. This discrepancy is investigated further in Section 3.3 and illustrates the sheer magnitude at which these marine CDR plants will operate.

3.3 Economic Analyses of Water Electrolysis & BPMED

3.3.1 Water Electrolysis Producing Solid $CaCO_3$

Figure 13 in Appendix B.3 illustrates a process flow diagram of the ideal sCS^2 water electrolysis process at commercial-scale. This process features upstream feed from a desalination plant based on the aforementioned process efficiencies and economic benefits of co-location.[13,14] With a DIC level of 6 mM and an overall capture efficiency of 80%, it was determined that this process requires a volumetric flow rate of 9.43 billion liters (59.3 million barrels) of brine per day to achieve the 1 Mt goal.

The Ras Al-Khair desalination plant, the largest in the world,[11,12] only produces about 11% of the brine required for this sCS^2 process daily, demonstrating that running desalination and sCS^2 in series is not feasible at this time. However, due to the massive economic benefits, it is assumed that an adequately sized desalination plant will be constructed in the future to properly feed this sCS^2 process at commercial-scale.

To calculate the required land area, the Ras Al-Khair desalination plant was used as a baseline, which has a total land area of 2 km^2 and takes in about 2.1 billion liters (13.2 million barrels) of seawater daily.[11,12] With a required brine feed volumetric flow rate of 9.43 billion liters (59.3 million barrels) per day, about 5x more than the daily feed to the Ras Al-Khair desalination plant, it is assumed the necessary upstream desalination plant will require about 5x more land area as well. This corresponds to a maximum land area of 10 km^2 for the desalination plant, which will be integrated with multiple sCS^2 plants to meet the annual production requirements.

With a maximum brine volumetric flow rate of 500 m^3 per day, 18,869 mesh-electrode units will be needed to handle the required 9.43 billion liters (59.3 million barrels) of brine per day.[23,25] Researchers also estimated that a maximum of 8,410 mesh-electrode units can be used per plant, which are limited by overall weight and land area.[25] Due to these limitations, it was calculated that at least three sCS^2 plants will be needed at scale to achieve the annual 1 Mt goal. For an evenly distributed design of electrode units across three plants, each plant should have 6,290 electrode units. One SJT vertical turbine pump can supply around 1,920 units,[36] so each plant will need approximately four pumps in parallel, each operating around 50% capacity.

Using the correlation between energy required and the volume percent of CO_2 in solution derived by the Institute for Carbon Management at UCLA,[25] the team estimated the energy requirement for the sCS^2 process to be 1.75 MWh per tonne CO_2 mineralized. Because H_2 gas is co-produced during this process and is assumed by the team to be re-electrified and recycled to power the process, this energy requirement can be offset by the energy intensity of H_2 gas generation, estimated to be between 0.8 - 1.2 MWh per tonne CO_2 mineralized.[34] This results in a total energy requirement around 0.55 - 0.95 MWh, which, with an assumed cost of electricity of \$40 per MWh,[14] corresponds to an overall electrical cost between \$22 - \$38 per tonne CO_2 mineralized.

Capital costs were estimated to be around \$500 per tonne CO_2 captured. The operating costs, which accounts for energy, fixed operations, and maintenance costs, were estimated to be around \$83 per tonne CO_2 captured.[25] Accounting for the recycled energy produced from H_2 gas, these operating costs are reduced to \$35 - \$51 per tonne CO_2 captured, giving an overall cost for the sCS^2 process of \$535 - \$551 per tonne CO_2 mineralized.

However, the team determined that this process only produces 0.83 tonnes of $CaCO_3$ per tonne of CO_2 captured, so the "true" overall cost for the process is around \$645 - \$664 per tonne $CaCO_3$ produced. Nevertheless, a lower overall cost arises from the alternate scenario in which all the co-produced H_2 gas is sold as a green fuel valued at \$3 per kg, resulting in a cost reduction of \$135 per tonne.[25] With a capital expense of \$365 per tonne and an operating cost of \$83, the overall cost is \$448 per tonne CO_2 mineralized. In terms of the carbonate product, the "true" overall cost for the process is around \$540 per tonne $CaCO_3$ produced. Comparing the cost ranges for both scenarios to the assumed selling price of \$336 - \$370 per tonne $CaCO_3$, the process is not considered to be economically viable at this time. The calculations for these values can be viewed in Appendix C.1.

Because the specialized electrolyzer units account for the majority of the overall costs, significant cost savings can be made by using cheaper cathode and anode materials.[25] Additionally, improving the capacity of the electrolyzer units would allow for lower pumping and piping costs, as well as higher throughput values. Water electrolysis represents an active area of research, so many lab-scale improvements are expected in the coming years. Ideally, these improvements can lower the overall cost for this process at commercial-scale below the assumed selling price of $CaCO_3$, allowing this process to be economically profitable.

3.3.2 BPMED Producing Solid $CaCO_3$

Figure 14 in Appendix B.3 details a potential process flow diagram for a BPMED process capable of removing 1 Mt of CO_2 from brine annually. For an assumed DIC level of 6 mM and an overall capture efficiency of 60% - 70%, 11.8 - 13.8 billion liters (74.2 - 86.8 million barrels) of brine will need to be processed daily.[13,14] As mentioned in Section 3.2, the largest desalination plant in the world is only capable of producing 1.04 billion liters (6.54 million barrels) of brine every day,[11,12] around 8% of the volume required by this marine CDR process. This shows that while coupling this CDR plant with a desalination plant is massively beneficial, it is not yet feasible at commercial-scale.

Because these marine CDR processes are significantly cheaper to operate while co-located with a desalination plant, the remainder of this economic analysis assumes that a hypothetical desalination plant exists that is large enough to partner with this CDR plant. The Ras Al-Khair desalination plant was used as a baseline, which takes in approximately 2.1 billion liters (13.2 million barrels) of seawater daily and has a 2 km^2 land area.[11,12]

Because this CDR plant will need to process a minimum of 11.8 billion liters (74.2 million barrels) of brine daily, approximately 8x more than the Ras Al-Khair desalination plant takes in now,[12] it is estimated that a hypothetical upstream desalination plant will require up to 8x more land area as well. This corresponds to a maximum land requirement of 16

km^2 for this desalination plant, which will be coupled with a comparably-sized marine CDR plant. To supply this process with brine, approximately six Sulzer SJT vertical turbine pumps will be needed in parallel, assuming each operates around 50% capacity.[36]

It is worth noting that a single BPMED unit is needed for this process, because multiple cell pairs can be repeated in parallel within the electrode pair to scale up the process. This can be done without significant voltage losses or unintended side reactions.[8,15] The industrial-size BPMED unit will operate with a current density of 2000 A/m^2, a voltage of 90 kV, a current efficiency of 75% - 85%, and a membrane area between 1.6 - 2 m^2.[20,21]

With these parameters, the BPMED energy requirement was calculated to be 1.61 - 2.29 kWh per kilogram $CaCO_3$. Using an electricity cost of \$40 per MWh,[13] and assuming the BPMED unit makes up 80% of the electricity requirement for the entire CDR plant,[13,14] the total electrical cost for the CDR plant was calculated to be \$81 - \$115 per tonne $CaCO_3$.

To estimate the total CDR plant costs for the BPMED process, it was assumed that the electrical costs made up about 20% of the total plant costs,[14,15] resulting in a final overall cost of \$405 - \$575 per tonne $CaCO_3$. Because the average selling price of $CaCO_3$ is assumed to be \$336 - \$370 per tonne, this process is not considered to be economically viable at this time. The calculations for these values can be viewed in Appendix C.2.

Because BPMED is still an active area of research, many technological improvements are expected in the near future. These improvements can include reduced costs of materials for the BPMED unit, improved membrane selectivities and current efficiencies, or optimized overall energy consumption values.[16,18] Currently, BPMED accounts for approximately 80% of the total electrical consumption for the entire CDR plant,[13,14] so optimizing its current efficiency or reducing its overall energy consumption would result in significant cost reductions. Ideally, these lab-scale investigations can decrease the overall cost of the process such that these commercial-scale marine CDR plants operate significantly below the assumed selling price of \$336 - \$370 per tonne $CaCO_3$.

3.4 CCU Value Chain

A potential CCU value chain can be described in five stages: source characterization, capture/separation, purification, storage/transportation, and utilization.[9] For both water electrolysis and BPMED, the source characterization of the captured carbon is upper ocean waters or brine from an upstream desalination plant. Section 3.2 details the many advantages of coupling these CDR processes with a desalination plant, such as reducing its overall costs and increasing the overall process efficiencies.[11,12]

Each technology has a similar capture/separation step, utilizing an *in-situ* electrochemical methodology to produce the necessary pH-swing to manipulate the thermodynamic equilibrium of dissolved CO_2 in seawater. The details for these methods are shown in Sections 2.1 and 2.2. At an alkaline pH, these processes effectively combine dissolved CO_3^{2-} ions with aqueous Ca^{2+} ions and precipitate solid $CaCO_3$ as the final product.[16,23]

The purification step is the same for water electrolysis and BPMED in terms of the recovered $CaCO_3$, where it is separated from the brine, cleansed of other co-precipitates if needed, and dried to increase downstream marketability.[10] One of the main dissimilarities to CO_2 production comes in this step, as the recovered $CaCO_3$ does not require additional, industry-specific purification before it can be sold downstream.[10] For water electrolysis, the co-produced H_2 gas likely will require downstream purification before it can be recycled back into the process or sold to industry as a green fuel.[25]

The storage/transportation step is much more streamlined for solid $CaCO_3$ production than for gaseous CO_2 production, exemplifying another major difference between the two processes. This is because when DIC is converted into solid $CaCO_3$ precipitate, it is considered to be in a permanent and stable form with no risk of leakage.[8,16] In so doing, the $CaCO_3$ can easily be stored on-site until it is utilized downstream.

The final step, utilization, is again mirrored between water electrolysis and BPMED for the recovered $CaCO_3$. As stated in Section 3.1, the team prioritizes supplying carbon-based products to industries that produce long-lived products to minimize re-emitting the recovered carbon back into the atmosphere.[10] For $CaCO_3$, the two target industries are cement and paper with attractively long-lived and easily-recyclable products, respectively.[8,16] For water electrolysis, the co-produced H_2 gas can be marketed to the energy sector as a green fuel or recycled back into the process, lowering its overall energy requirement.[23,25] Finally, the decarbonized seawater is returned to the oceans, where it is allowed to re-equilibrate with the atmospheric CO_2 before being used as desalination feedstock again.[8,16]

4 Marine CDR Environmental Effects

Because this paper proposes several *in-situ* electrochemical CDR pathways, it is extremely important to analyze any potentially adverse effects of this technology once incorporated at scale. Obviously, marine wildlife are most immediately affected by the utilization of these technologies, so they are a primary focus in analyzing its overall feasibility. The Energy Futures Initiative warns of several negative repercussions of employing these marine CDR plants at commercial-scale; physically trapping animals in industrial-sized machinery, inadvertently disturbing marine habitats and movement patterns, or even irreversibly changing ocean biochemistry from increased ocean alkalinity.[7]

Additionally, it is critical to acknowledge the impact on nearby coastal communities, as it affects their perceptions of CDR technology as a whole. Because of their location, many of these cities will rely heavily on maritime activities, such as shipping, fishing, or tourism, to support their local economies.[7] Ideally, marine CDR plants will synergize with these existing assets by reducing thermal and chemical stresses on the oceans. According to the Energy Futures Initiative, public acceptance of these technologies is imperative to their success, as many large-scale research projects have been abandoned due to social unrest.[7]

As for the oceans themselves, the team recognizes that a significant reduction in Ca^{2+} and Mg^{2+} ion concentrations in the oceans may be destructive to marine wildlife. A research team from Hebei Institute of Technology projected a parts per million change in Ca^{2+} and Mg^{2+} concentrations using their *in-situ* mineralization method at scale, ultimately resulting in negligible ecological effects.[17] However, as their work was only completed at lab-scale, their results are considered to be inconclusive and represent an area of active research.

To help mitigate the ecological risks, whose effects are still largely uncertain at this time, it is suggested to potentially deploy these marine CDR plants in areas with smaller marine and human populations. However, this may present an economic/moral trade-off, as many of the largest desalination plants in the world are placed near heavily-populated areas to supply large volumes of fresh water.[11,12] As stated in Section 3.2, co-location of these marine CDR plants with existing desalination plants have massive economic benefits and greatly reduces the costs of their implementation at scale.

5 Conclusions & Recommendations

The world has been experiencing deleterious environmental effects over the past few decades, largely due to increased atmospheric CO_2 concentrations.[1–6] The team analyzed two *in-situ* electrochemical CDR methods, water electrolysis and BPMED, that can effectively lower emissions by removing carbon from seawater.[8,16] In general, water electrolysis was determined to have higher energy requirements and overall expenses, but also had larger downstream economic opportunity due to the co-production of H_2 green fuel.[23,25] BPMED has lower energy requirements and capital and operating costs, but relies on the downstream marketability of CO_2 or $CaCO_3$ to remain economically viable.[14,16] It will be left up to potential investors as to which technology suits their needs better, as both are conceptually viable and have distinct strengths and weaknesses.

While both gaseous CO_2 and solid $CaCO_3$ can be produced from these techniques, the team recommends operating these electrochemical CDR methods at an alkaline pH to produce the latter. This is because solid $CaCO_3$ as the final product results in lowered capital and operating costs, more straightforward handling and storage, and increased downstream marketability.[10,19] Furthermore, the team heavily recommends co-locating the marine CDR plant with an upstream desalination plant if possible to avoid the massive costs of pumping, pretreating, and piping large volumes of seawater.[7,14]

At commercial-scale, the water electrolysis process is estimated to operate at an overall cost of $448 - $551 per tonne CO_2 captured, with cost improvements coming from selling the co-produced H_2 gas downstream rather than recycling it back into the process. This corresponds to a "true" overall cost $645 - $664 per tonne $CaCO_3$ produced. Likewise, the team found that a scaled-up BPMED process will operate at an overall cost of $405 - $575 per tonne $CaCO_3$ produced. For an assumed selling price range of $336 - $370 per tonne $CaCO_3$, it was determined that neither of these technologies are economically viable at this time. Moreover, because the team estimates that these marine CDR technologies will not be commercially-viable for several decades, it is assumed that their large energy requirements can be offset by large-scale utilization of renewable energies, promoting a circular economy and producing net-negative carbon emissions.[8,16]

In addition to the dubious economic benefits from these marine CDR technologies at this time, there are still high levels of uncertainty surrounding their ecological effects at commercial-scale. This is because there are no current large-scale marine CDR facilities, which prevents accurate analyses of any unintended environmental side-effects.

Overall, the team has concluded that these marine CDR technologies are conceptually viable and can effectively lower atmospheric CO_2 emissions by removing carbon from seawater. However, they are not economically viable at this time, at least by only using the marketability of $CaCO_3$ and/or H_2 gas as the sole source(s) of income. Because of this, the team suggests that these technologies be employed once the bulk of the CO_2 emissions have been removed, as they can be used to achieve the final, most difficult separations.[8,16] Despite the ambitious goal 10 Gt goal posed by the Paris Agreement,[7,8] the team remains optimistic that it can be achieved to effectively address the current climate change crisis.

6 Future Plans

The future plans for this project include reinvestigating the technological and economic viability of these *in-situ* electrochemical CDR technologies at commercial-scale once significant technological improvements have been made at lab-scale. Because water electrolysis and BPMED are active areas of research, the team believes that these lab-scale improvements can be made reasonably quickly, allowing for commercial-scale deployment by 2050.

As mentioned in Section 3.3, these lab-scale improvements ideally should include lowered overall energy requirements, as the electrical requirements for these *in-situ* electrochemical techniques make up a large portion of the overall cost of the CDR plants at commercial-scale. Another significant area of improvement could be to increase the overall process efficiency. This would allow these marine CDR plants to process smaller volumes of seawater/brine, potentially allowing co-location with existing desalination plants.

Finally, the team acknowledges that the cost estimation of these CDR technologies at scale carries a large degree of uncertainty, as there are no current large-scale marine CDR plants to base the calculations on. If the timeline for this project were extended, the team would explore life-cycle analyses, process safety analyses, and specific unit operation estimations for the CDR facility to refine capital and operating expenditure calculations. It may also be beneficial to investigate supplementary funding, such as governmental subsidies or co-financing from high-emissions companies, that would allow these processes to not rely solely on the downstream marketability of $CaCO_3$ to remain economically viable.

Appendix

A: Project Charter

1. General Project Information	
Project Name:	Ocean-Based Carbon Dioxide Removal
Executive Sponsors:	Chevron Corporation
Department Sponsor:	Purdue University Davidson School of Chemical Engineering
Impact of Project:	Investigate and propose practical CDR technologies for use in a marine environment

2. Project Team			
	Name	**Telephone**	**Email**
Project Mentor:	Dr. Hariprasad J. Subramani	(713) 372-3133	hjsubramani@chevron.com
Project Manager:	Dr. William R. Clark	(317) 691-1438	clarkw@purdue.edu
Project Member:	Daniel Ciuca	(614) 582-8217	dciuca@purdue.edu
Project Member:	Vincent Valbuena	(806) 886-3246	vvalbuen@purdue.edu

3. Stakeholders
Chevron Corporation - Industry Partner
Purdue University - Educational Partner

4. Project Scope Statement
4.1 Project Purpose
The purpose of this project is to research marine CDR technologies and develop a thorough understanding of their functionalities and their unique safety/environmental concerns, perform an economic analysis and investigate potential value chain(s) for these technologies, and provide a final recommendation for an optimal technology.
4.2 Objectives
The objectives of this project are to develop a thorough understanding of marine CDR technologies and their safety/environmental concerns as well as recommend an optimal marine CDR technology with a potential value chain to maximize economic viability.
4.3 Deliverables
The deliverables of this project are a final manuscript detailing the need for marine CDR, proof of concepts for various CDR technologies, unique safety/environmental concerns, and an economic analysis including potential value chain opportunities. These findings will be summarized in a final presentation to be held on August 3rd.
4.4 Scope
This project will investigate marine CDR methods such as *in-situ* electrochemical pathways including pH-swing techniques such as water electrolysis and bipolar membrane electrodialysis (BPMED), ecological pathways including artificial upwelling/downwelling that can be utilized upstream, and the economics related to each topic.
4.5 Project Milestones
5/18 – 6/3 Understand Project Expectations and Complete Project Charter 6/4 – 6/11 Individually Review Information on Electrochemical Technologies 6/12 – 6/20 Complete Write-Up on Electrochemical Technologies, Complete Introduction 6/21 – 7/3 Complete Write-Up on Other Technologies

7/4 – 7/20 Perform Economic Analyses, Complete Write-Up 7/21 – 7/24 Perform Safety Analyses, Complete Write-Up 7/25 – 8/1 Final Revisions, Submit Final Manuscript to Brightspace 8/1 – 8/3 Practice and Prepare for Oral Presentation
4.6 Important Dates
5/18 – Introduction to the Semester 5/26 – Project Charter & Team Agendas Overview 6/6 – Technical Meetings w/ Dr. Clark 6/6 – Introduction to Technical Writing 6/13 – Writing Assignment Due 6/15 – Indv. Writing Meetings and Workshops 6/20 – Technical Meetings w/ Dr. Clark 6/27 – Introduction to Oral Presentations 6/30 – Mini Oral Presentations and Meetings 7/4 – Independence Day 7/11 – Technical Meetings w/ Dr. Clark 7/25 – Open Office Hours 8/1 – Final Manuscripts Due 8/3 – Final Presentations
4.7 Major Known Risks
Insufficient access to necessary literature, specifically pertaining to economic evaluations of CDR technology – Low
4.8 Constraints
The time duration of this project is constrained between May 18 and Aug. 5, 2022, with the final oral presentation to be given between Aug. 3 and Aug. 5, 2022. Due to distance constraints, communications with the Project Mentor will take place entirely via email and Zoom/Teams. Furthermore, this project is entirely academic/theoretical and consequently will have a monetary budget of $0 and will be restricted to two Purdue PMP students under the supervision of the Project Manager, Dr. William R. Clark, and the Project Mentor, Hariprasad Subramani.
4.9 External Dependencies
The outcome of this project will depend on sufficient access to online resources such as published research with proven scale-up potential and economic viability for each CDR method. Additionally, the outcome of this project will depend on timely communication between Team Members and the Team Mentor.
4.10 Resources
This project will utilize various online journals/articles on marine CDR topics as well as any resources available to the Davidson School of Chemical Engineering. All other necessary resources will be provided by the Project Mentor from Chevron Corporation. This project is entirely academic and will have a monetary budget of $0.

5. Communication Strategy
Communication between the Project Mentor and the Project Members will take place via email and biweekly Zoom/Teams meetings on Fridays at 1:30pm EST. Communication between the Project Manager and the Project Members will take place via email and biweekly meetings in-person. Communication between Project Members will take place over text and email, as well as recurring meetings over Zoom as needed.

6. Sign-off

	Name	Signature	Date
Project Mentor:	Dr. Hariprasad J. Subramani	Hariprasad J. Subramani	06/30/2022
Project Manager:	Dr. William R. Clark		
Project Member:	Daniel Ciuca	Daniel Ciuca	5/31/2022
Project Member:	Vincent Valbuena	Vincent Valbuena	5/31/2022

B: Graphs & Figures

B.1: Environmental Effects due to Climate Change

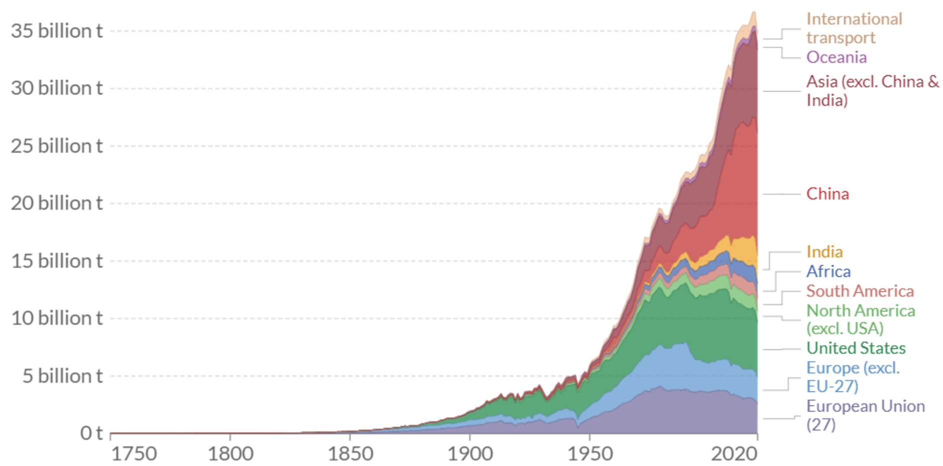

Figure 3: Global CO_2 Emissions by World Region

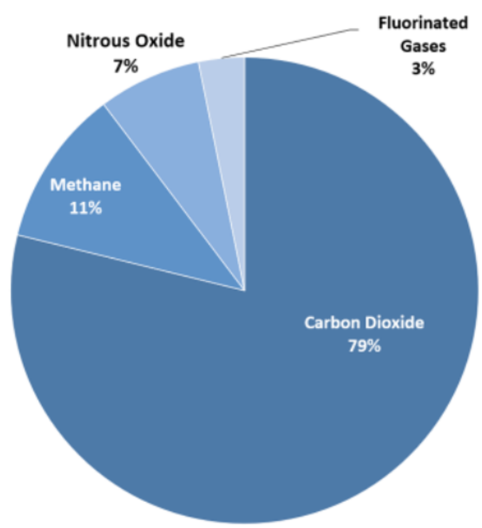

Figure 4: Global GHG Emissions by Gas Type

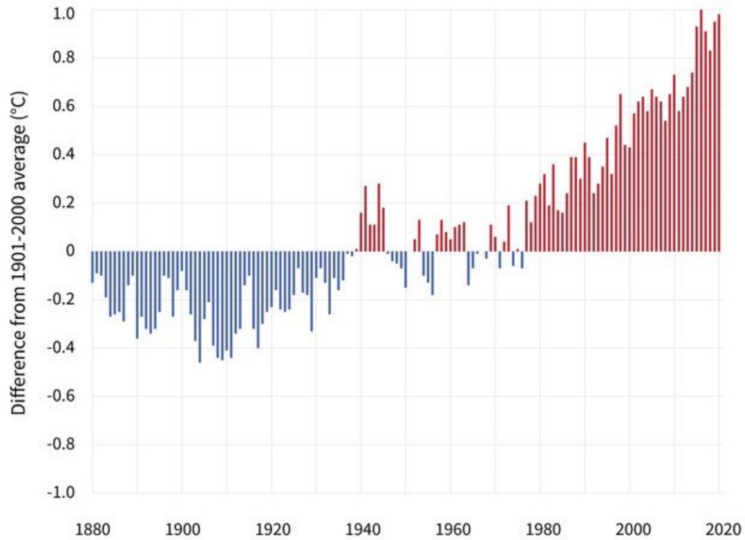

Figure 5: Global Temperatures Since 1880

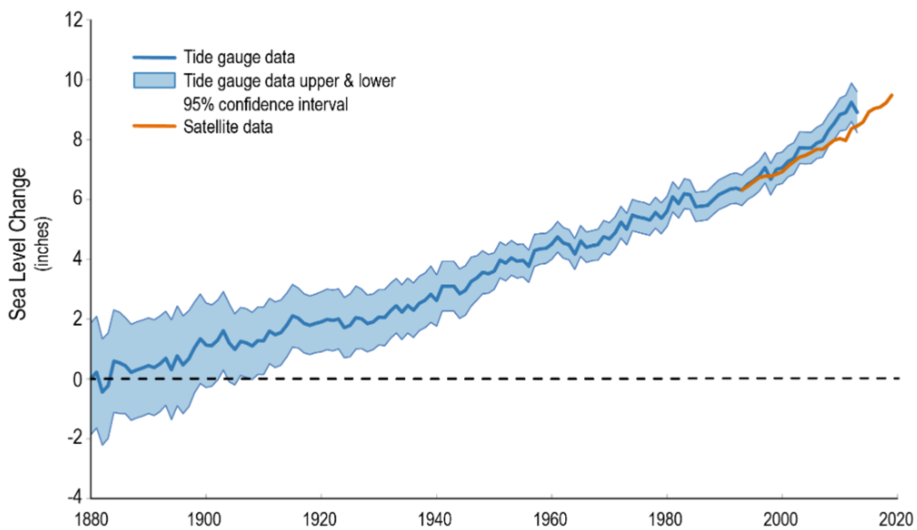

Figure 6: Global Sea Levels Since 1880

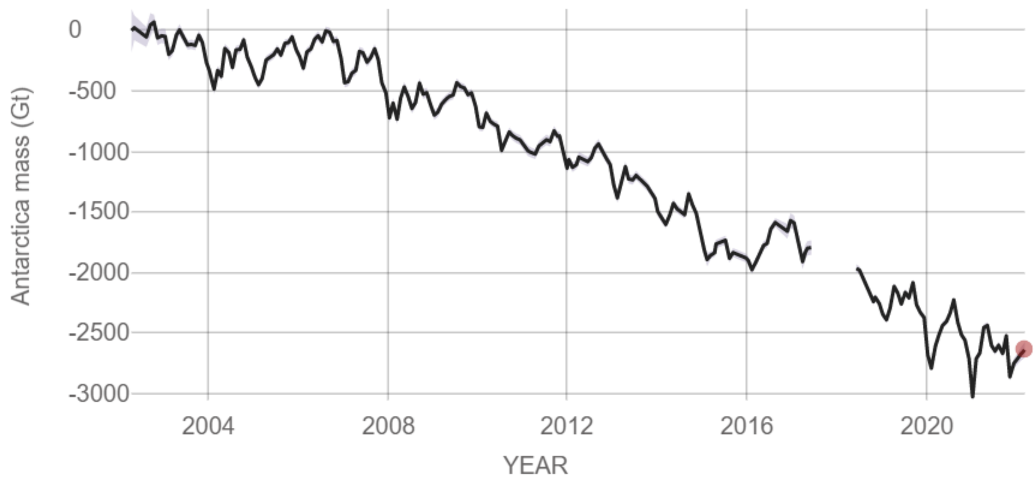

Figure 7: Antarctic Ice Mass Since 2002

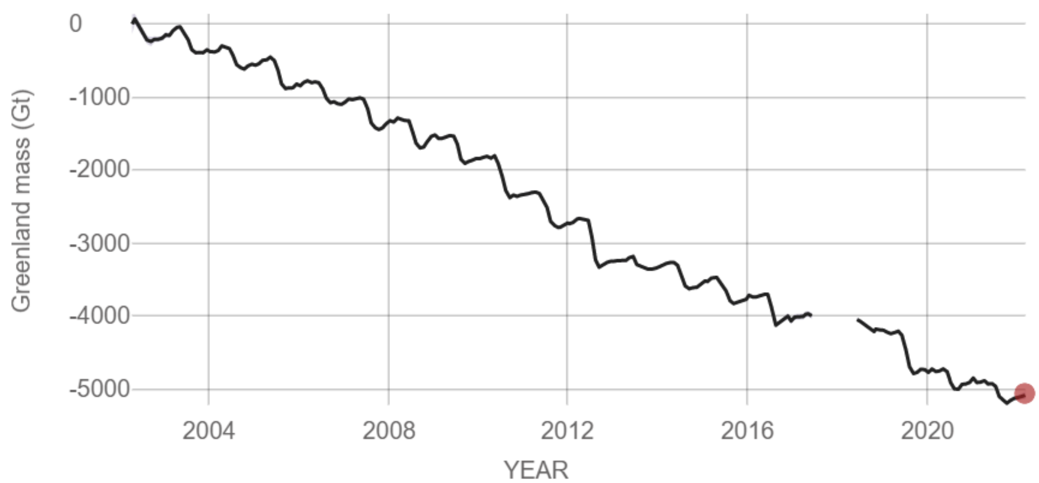

Figure 8: Greenland Ice Mass Since 2002

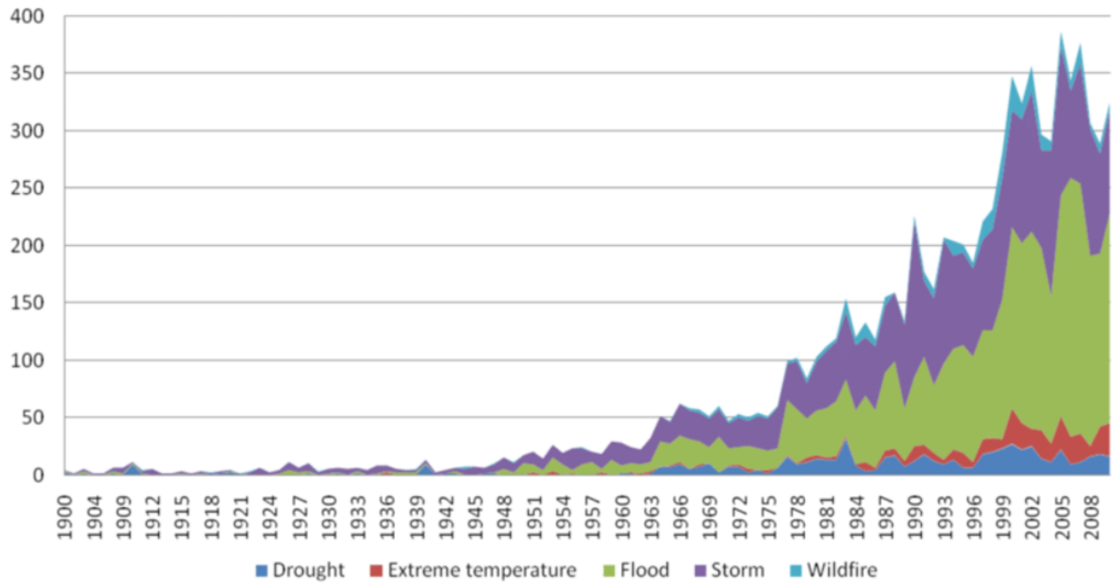

Figure 9: Global Extreme Weather Events Since 1900

B.2: Experimental Setups for Lab-Scale CDR

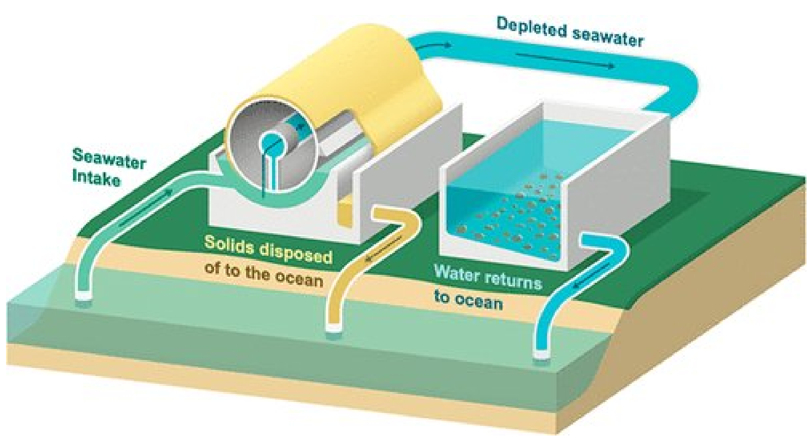

Figure 10: sCS^2 Schematic For CO_2 Mineralization

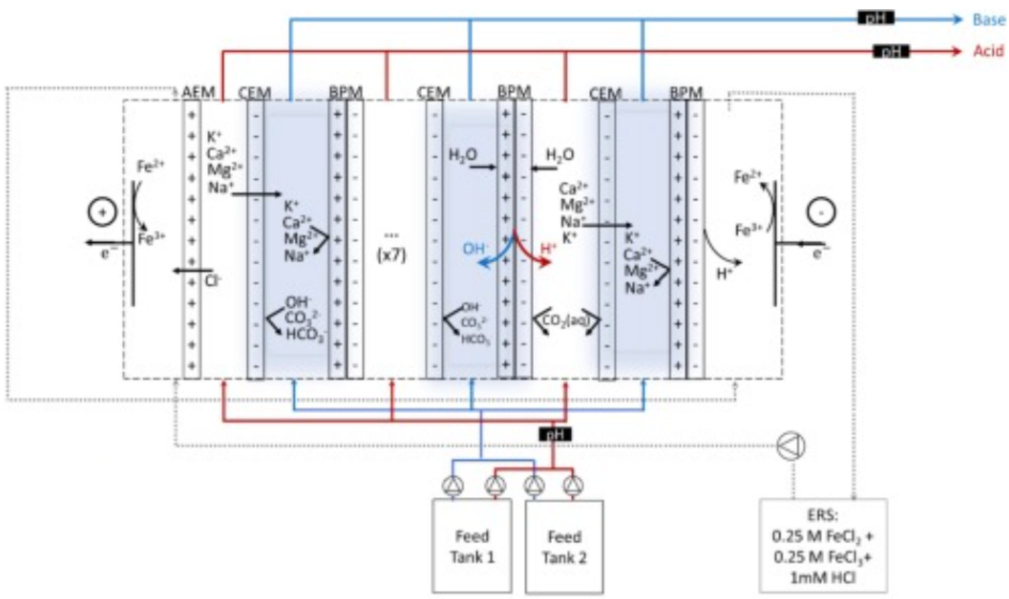

Figure 11: Experimental BPMED Setup for Sharifian et al.

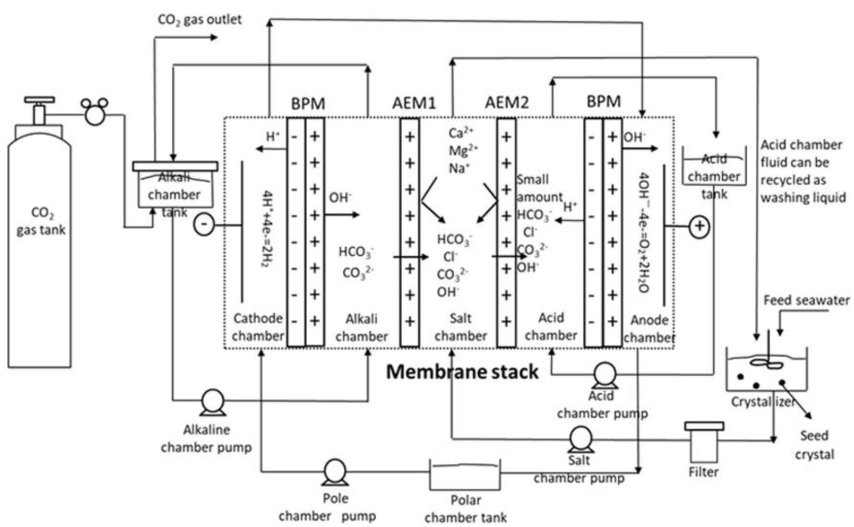

Figure 12: Experimental BPMED Setup for Zhao et al.

B.3: Process Flow Diagrams for Commercial-Scale Marine CDR

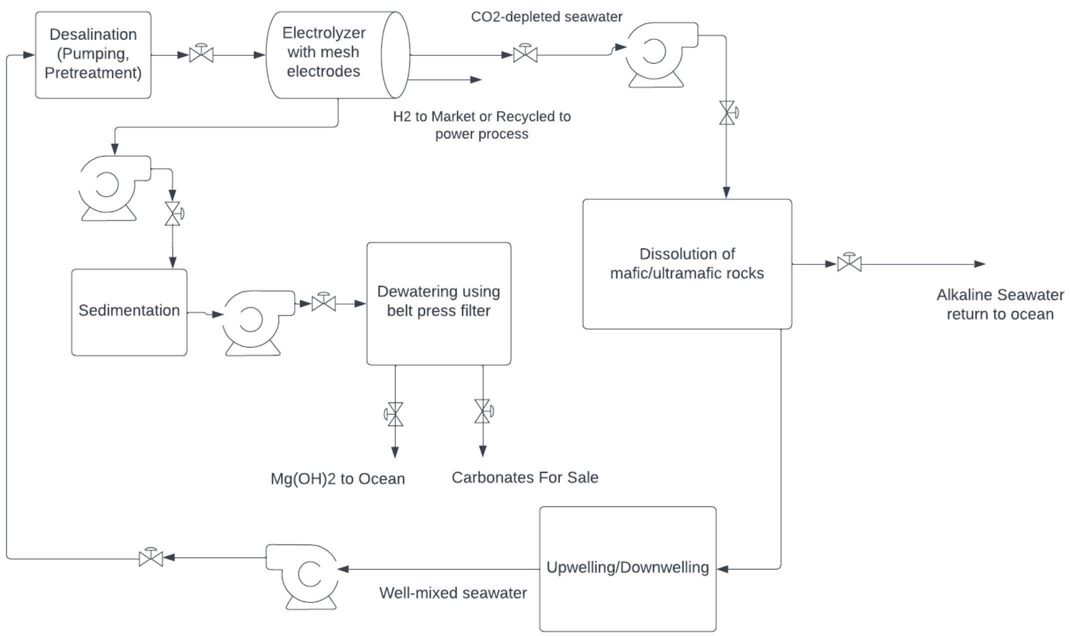

Figure 13: Sample Water Electrolysis Process Flow Diagram

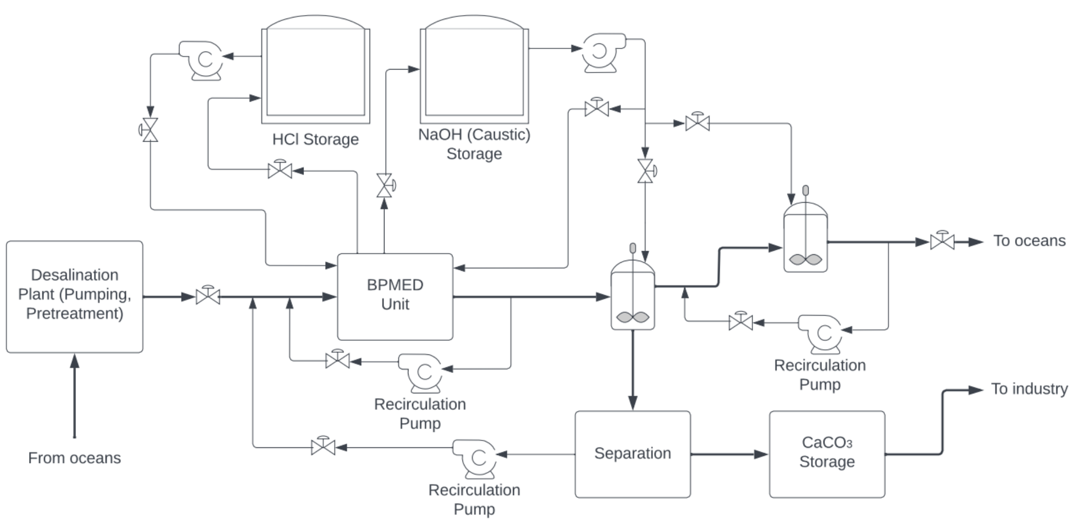

Figure 14: Sample BPMED Process Flow Diagram

C: Sample Calculations

C.1: Water Electrolysis Economic Analysis Calculations

$$\frac{6\ mmol\ DIC}{L\ brine} * \frac{60.5\ mg\ DIC}{mmol\ DIC} * \frac{g\ DIC}{1000\ mg\ DIC} * \frac{kg\ DIC}{1000\ g\ DIC} = 3.63e^{-}4\ \frac{kg\ DIC}{L\ brine} \quad (6)$$

$$M_{DIC} = 1e9\ \frac{kg\ DIC}{yr} * \frac{yr}{365\ days} = 2.74e6\ \frac{kg\ DIC}{day} \quad (7)$$

$$\frac{2.74e6\ kg\ DIC}{day} * \frac{100.1\ kg\ CaCO_3}{60.5\ kg\ DIC} * \frac{0.5}{1} * \frac{1\ Mt}{1e9\ kg} * \frac{365\ days}{1year} = 0.83\ \frac{Mt\ CaCO_3}{year} \quad (8)$$

$$2.74e6\ \frac{kg\ DIC}{day} * \frac{L\ brine}{3.63e^{-}4\ kg\ DIC} * \frac{1}{0.8} = 9.434e9\ \frac{L\ brine}{day} \quad (9)$$

$$9.434e9\ \frac{L\ brine}{day} * \frac{m^3}{1000\ L} * \frac{units}{500\ m^3/day} * \frac{plant}{8,410\ units} = 3\ plants \quad (10)$$

C.2: BPMED Economic Analysis Calculations

$$\frac{1,000,000\ tonne}{year} * \frac{1000\ kg}{tonne} * \frac{year}{365\ days} \approx 3e6\ \frac{kg\ DIC}{day} \quad (11)$$

$$\frac{3e6\ kg\ DIC}{day} * \frac{100.1\ kg\ CaCO_3}{60.5\ kg\ DIC} * \frac{day}{24\ hr} \approx 2.1e5\ \frac{kg\ CaCO_3}{hr} \quad (12)$$

$$\frac{6\ mmol\ DIC}{L\ brine} * \frac{60.5\ mg\ DIC}{mmol\ DIC} * \frac{g\ DIC}{1000\ mg\ DIC} = 0.363\ \frac{g\ DIC}{L\ brine} \quad (13)$$

$$\frac{3,000,000\ kg}{day} * \frac{1000\ g}{kg} * \frac{L\ brine}{0.363\ g\ DIC} * \frac{1}{0.6\ (0.7)} = 1.38e10\ (1.18e10)\ \frac{L\ brine}{day} \quad (14)$$

$$\frac{2000\ A}{m^2} * \frac{2\ (1.6)\ m^2}{1} * \frac{90\ kV}{1} * \frac{hr}{2.1e5\ kg} * \frac{1}{0.75\ (0.85)} = 2.29\ (1.61)\ \frac{kWh}{kg} \quad (15)$$

$$2.29\ (1.61)\ \frac{kWh}{kg} * \frac{1}{0.8} * \frac{1000\ kg}{tonne} * \frac{1\ MWh}{1000\ kWh} * \frac{\$40}{MWh} = \frac{\$115\ (\$81)}{tonne} \quad (16)$$

$$\frac{\$115\ (\$81)}{tonne} * \frac{\$5\ total\ plant\ costs}{\$1\ electrical\ costs} = \frac{\$575\ (\$405)}{tonne} \quad (17)$$

D: Notation

Symbol	Description
AEL	Anion-Exchange Layer
BPM	Bipolar Membrane
BPMED	Bipolar Membrane Electrodialysis
CCS	Carbon Capture and Storage
CCU	Carbon Capture and Utilization
CDR	Carbon Dioxide Removal
CEL	Cation-Exchange Layer
DAC	Direct Air Capture
DIC	Dissolved Inorganic Carbon
E-CEM	Electrolytic Cation-Exchange Module
GHG	Greenhouse Gas
Gt	Gigatonne (1 billion tonnes)
Mt	Megatonne (1 million tonnes)
OER	Oxygen Evolution Reaction
sCS^2	Carbon Sequestration and Storage
STP	Standard Temperature and Pressure

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