Article

Managing CO$_2$ levels through precipitation-based capture from seawater and electrochemical conversion

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SUMMARY

With the rise in global greenhouse gas emissions, many studies have sought methods to reduce the accumulation of carbon dioxide (CO$_2$) in the atmosphere. Existing methodologies are primarily based on amine solvents such as monoethanolamine (MEA) and 2-amino-2-methylpropanol (AMP) due to their high carbon absorption capacity and good recyclability. As such, they are used for the capture of CO$_2$ from sequestration sites and its subsequent electrochemical transformation. However, because amines have large enthalpies of reaction, this leads to expensive and energy-intensive processes that limit their capacity for large-scale application. Thus, this study seeks to develop an electrochemical device that can sustain efficient CO$_2$ capture and conversion through precipitation. The dissolved inorganic divalent cation calcium (Ca^{2+}) reacts with carbon to form carbonate (CO$_3^{2-}$) compounds that flow through a thin membrane, facilitating the filtration of the precipitate. We hypothesized that higher alkalinity will produce a greater quantity of CO$_2$ capture, as measured by the change in seawater pH and the mass of precipitate formed. The CO$_3^{2-}$ compound is, in turn, converted to the industrial fuel formic acid (HCOOH). Through our experimentation, we found a statistically significant difference between the measured pH of seawater before and after CO$_2$ capture ($p<0.001$), thus suggesting this setup as a proof of concept for the effective reduction of ocean acidification. Additionally, we observed an upwards trend as higher concentrations of sodium hydroxide (NaOH) were generally associated with greater changes in pH.

INTRODUCTION

In 2019, an estimated 36.7 gigatons of carbon dioxide (CO$_2$) were emitted globally from burning fossil fuels and other industrial processes (1). The emissions of greenhouse gasses have accelerated global warming and climate change as well as harmed ecological systems such as oceans, which absorb excess CO$_2$ from the atmosphere (1). As CO$_2$ dissolves in H$_2$O to create carbonic acid (H$_2$CO$_3$), the weak acid will dissociate into hydrogen ions (H$^+$) and bicarbonate (HCO^{3-}). This process is known as ocean acidification. The issue arises when the H+ ions bond with carbonate ions (CO$_3^{2-}$) present in the water, leaving less CO32- available for the many marine creatures who depend on it to build their calcium carbonate (CaCO$_3$) skeletons and shells. Over the past century, the average pH of seawater has decreased from 8.2 to 8.1, which on the logarithmic scale, represents a 30% increase in acidity (2). Thus, as levels of calcium carbonate minerals (aragonite and calcite) diminish, this significantly reduces the strength and proper shape of shells in various species, including but not limited to, sea urchins, pteropods, oysters, and sand dollars (3). To quantify this reduction in strength, Kroeker *et al.* measured the biological response of several taxonomic groups to a < 0.5 unit reduction in mean seawater pH (4). For mollusks (e.g., pteropods and oysters), they recorded a change of -40% calcification, -34% survival, and -25% development; for echinoderms (e.g., sea stars and sand dollars), the observed change was -10% growth and -11% development (4). This is significant because the observed market loss of reduced shellfish production is estimated to be 25 to 99 million dollars (5). Overall, by harming marine life and limiting the oceans' ability to absorb CO$_2$, ocean acidification exacerbates the already pressing issue of global warming, which has caused the global average temperature to increase by approximately 1.9oC since 1900 (6). In order to limit its further growth, 10 to 20 gigatons of CO$_2$ need to be removed from the atmosphere at an annual rate (7).

Many scientific solutions have focused on capture from seawater for CO$_2$ removal as oceans are one of Earth's largest carbon sinks, absorbing an estimated 26% of annual CO$_2$ emissions, or approximately nine gigatons (8). Since water contains nearly 150 times more CO$_2$ than air per unit volume, it offers a much more effective method of removing the gas (6). These proposed solutions rely on precipitation-based mineralization and electrochemical conversion into higher energy organic molecules such as carbon monoxide (CO), formic acid (HCOOH), or methanol (CH$_3$OH), some of which can then be harnessed in hydrogen-powered fuel cells. For instance, researchers at Rice University built an electrocatalysis reactor that transforms CO$_2$ into purified HCOOH (9). They observed an energy conversion efficiency of 42%, meaning that almost half of the electrical energy could be stored as a viable source of liquid fuel used to power an engine (9). This development is significant as it not only recycles the amount of carbon in the atmosphere but helps alleviate the energy crisis by providing a cost-effective source of energy and a clean place to store it. Currently, electrochemical conversion is completed in H-type cells, which facilitate the flow of CO$_2$ gas into the cathodic compartment, where the working electrode and reference electrode are set, before its movement into a gas chromatograph (GC) to detect and analyze gas products (10). One study conducted by Zhao and Wang observed a 91% formate Faraday's Efficiency (FE) at 15 mA cm-2 current density with the use of Tin (Sn) as a catalyst (11). Because of its versatility for various catalyst
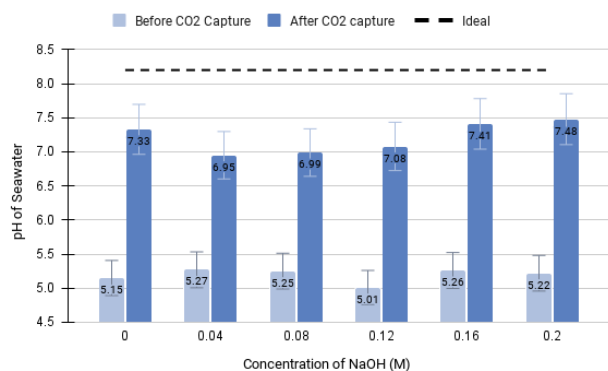
Figure 1: The measured pH of seawater before and after CO$_2$ capture with varying NaOH concentration (M) compared to the restoration goal, the ideal pH of seawater 8.2 (n = 6). The SEM error bars were calculated with a 95% confidence interval.
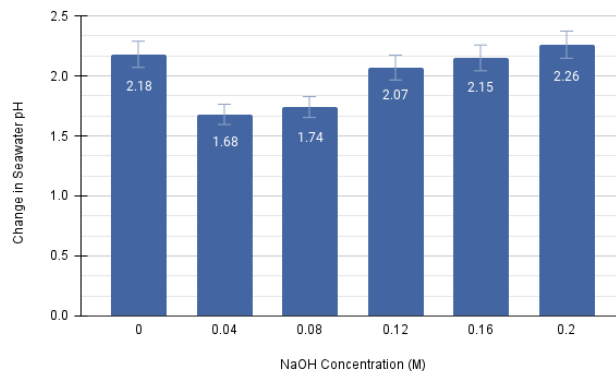

Figure 2: The effect of varying NaOH concentration (M) on the change in seawater pH due to precipitate-based capture (n = 6). The SEM error bars were calculated with a 95% confidence interval.

electrodes, H-type cells have been the conventionally used electrolyzer for CO$_2$RR products. However, the low aqueous solubility of CO$_2$ and limitation of mass transport of hydroxide (OH-) significantly limit its productivity. As a result, many research studies have sought to develop alternative methods of electrolysis for commercial application (12).

This research study set out to design and build a water electrolyzer unit that can capture CO$_2$ from seawater and convert it to useful fuels such as HCOOH in a manner that is sustainable, efficient, and economically feasible for large-scale industrial application. Furthermore, we investigated the effect of alkalinity on precipitation during capture as well as the effect of voltage on the formation of HCOOH during conversion. We hypothesized that higher alkalinity would result in a greater yield of CaCO$_3$ and thus larger increases in seawater pH. The data from our study demonstrated that precipitation-based mineralization is an effective approach for capturing and converting CO$_2$. With a more thorough evaluation, this approach has the potential to be developed for large-scale carbon management.

RESULTS
CO2 Capture

In this experiment, we investigated the possibility of reducing ocean acidification through precipitation-based capture. Additionally, we examined the effect of alkalinity on the change in seawater pH and the amount of precipitate produced. We then compared the data for these two dependent variables with the ideal pH of seawater (8.2) and 100 percent CaCO$_3$ yield (0.92 g). We added sodium hydroxide (NaOH) to the seawater solution in order to manipulate the independent variable of alkalinity. This strong base dissociates completely in an aqueous solution and releases OH$^-$ ions which increases the pH of the seawater by a factor dependent on its concentration. A total of six trials was set up with varying NaOH concentrations, ranging from 0.04 M to 0.2 M. This solution was added to carbonated water, which was used to simulate seawater. A digital pH meter was then used to record the pH of the seawater before and after the reaction. The paired t-test demonstrated no overlap in standard error of the mean (SEM) error bars and $p < 0.001$ using a 95% confidence interval (Figure 1). Since the p value is less than 0.05, this

illustrates a statistically significant difference between the two groups and thus an effective reduction in acidification. To determine the effect size, we compared the differences in the mean and calculated a Cohen's d value of 0.336, representing a small to medium effect. After confirming the potency of the precipitation method, we analyzed the relationship of NaOH concentration with both the change in pH and the mass of precipitate, observing that both relationships were directly proportional. Although the majority of trials supported this trend, exceptions included the first trial (0.00 M), which demonstrated a greater change in pH than what would have corresponded with the trend (Figure 2) and the third trial (0.08 M), that demonstrated a lower mass production of CaCO3 (Figure 3). Statistical analysis was completed by applying a linear regression model. We observed a moderate and positive correlation between alkalinity and change in pH (R = 0.4699) in which the variance in final concentration of NaOH added explains 22.1% of the change in pH. This correlation was also noted between alkalinity and mass of precipitate formed (R = 0.8498).

Electrochemical Conversion

In a subsequent trial, we tested the effect of voltage potential on the rate of HCOOH formation, which was measured through current density. We set up a CO$_2$-based electrolyte bath with commercial electrodes and Sn as the catalyst and performed a total of seven trials. We found that larger applied voltage (less negative) led to lower current densities, thus illustrating an inverse relationship between the two variables (Figure 4). A quadratic model was applied to the data, resulting in an RMSE value of 0.00742. This signifies a statistically significant difference.

DISCUSSION

In our experiments, we investigated the effect of alkalinity on precipitation during CO$_2$ capture and the effect of voltage on the formation of HCOOH during CO$_2$ conversion. We found a significant increase in seawater pH, as the differences in pH before and after CO$_3^{2-}$ mineralization were statistically significant ($p<0.001$), supporting our hypothesis that precipitation is a viable pathway for effective CO$_2$ capture. Therefore, this study serves as a proof of concept for the
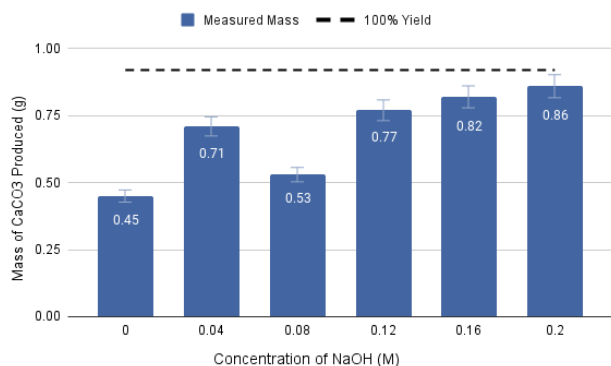
Figure 3: The effect of varying NaOH concentration (M) on the mass of CaCO3 precipitate produced (g) (n = 6). These values are also compared to 100% theoretical yield (0.92 g). The SEM error bars were calculated with a 95% confidence interval.
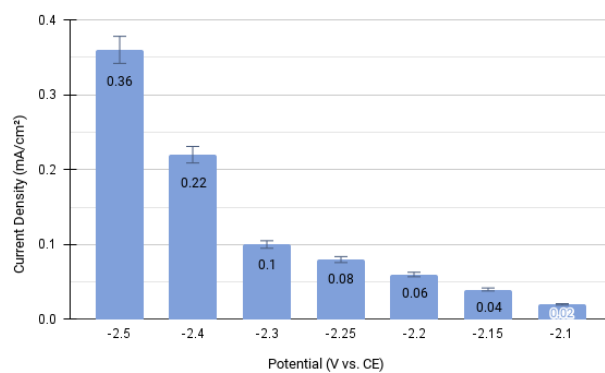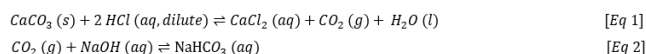

Figure 4: The effect of applied voltage potential on current density, which corresponds to the rate of HCOOH formation during electrochemical conversion (n = 7). CE represents the counter electrode. The SEM error bars were calculated with a 95% confidence interval. No overlap was observed in any of the trials.

removal of atmospheric CO_2 from seawater and neutralization of ocean acidity by HCOOH precipitation.

Our hypothesis that an increase in alkalinity would directly correlate to an increase in the change of pH and mass of precipitate formed was also supported, as shown by the paired t-test ($p<0.001$). However, we must also consider inconsistencies in the trials due to the experiments being conducted in a residential setting. For instance, there may have been fluctuations in room temperature or pressure during the period in which the beakers were left unattended, even though they were monitored to the best of our ability with a thermometer and barometer. These varying conditions could have affected the rate of the chemical reaction for each trial and whether they were fully driven to completion. Therefore, factors other than the one being tested, NaOH concentration, may have had an impact on the measured change in pH and mass of precipitate formed, thus contributing to a weaker correlation. Other possible limitations include impurities in the precipitate product ($CaCO_3$) such as undissolved calcium hydroxide ($Ca(OH)_2$) or outside air pollutants. This would have also affected the mass of precipitate and the observed relationship between the dependent and independent variable. However, this factor could be taken into consideration in a laboratory with quantitative NMR (Nuclear Magnetic Resonance) spectroscopy to assess the purity of the sample. If the samples were demonstrated to be impure, we could use techniques such as rotary evaporation to separate excess solvents from the desired product.

This method of precipitation-based CO_2 capture can potentially be applied to a larger-scale industrial setting after several adjustments. For example, rather than manually stirring the solution in glass beakers, agitation equipment would pump the seawater into large tanks and mix it with NaOH and $Ca(OH)_2$. Moreover, further research could be conducted to investigate the effect of other variables on change in pH and mass of precipitate, including temperature, type of base, or type of salt. We selected $Ca(OH)2$ for our experiment because of its more favorable reaction and greater thermodynamic stability compared to other divalent CO_3^{2-} compounds such as $MgCO_3$ (13). Nonetheless, examining these additional elements would enhance the breadth of the study and help determine the most favorable conditions for effective precipitation-based capture. Particularly, alternate strong bases could be used, such as KOH and $Ba(OH)_2$, which will behave similarly to NaOH.

A theoretical intermediary reaction was included between CO_2 capture and conversion in order to set up the next step by transforming $CaCO_3$(s) into $NaHCO_3$. This is shown in the following series of reaction steps.

$$CaCO_3\ (s) + 2\ HCl\ (aq, dilute) \rightleftharpoons CaCl_2\ (aq) + CO_2\ (g) + H_2O\ (l) \qquad [Eq\ 1]$$

$$CO_2\ (g) + NaOH\ (aq) \rightleftharpoons NaHCO_3\ (aq) \qquad [Eq\ 2]$$

Regarding electrochemical conversion, we demonstrated that electrolysis could be performed using a CO_2-based electrolyte bath and commercial electrodes. The current we measured represents the rate at which electric charge flows through a circuit, thus corresponding to the rate of reaction at the electrode surface. From our data, we observed that a smaller difference in charge between the working electrode (cathode) and counter electrode (anode) is associated with a lower rate of HCOOH formation. This supports our hypothesis that current density is proportional to applied voltage potential, specifically in a quadratic rate. However, it is unclear if HCOOH was the only product created or if there were side reactions as we did not have access to a gas chromatograph (GC) to detect the presence of other compounds. With every additional product, such as H_2 or CO, the total rate is reduced, and a smaller mass of desired product (HCOOH) is made. In order to resolve this, laboratory analytical techniques such as gas chromatography or mass spectrometry can be used to analyze the content of the mixture. Furthermore, to investigate the possibility of secondary chemical reactions, the electrode should be tested in NaOH solution with no CO_2.

Overall, our research study demonstrates that further investigation should be conducted to determine whether precipitation-based capture and CO_3^{2-} mineralization is a viable method of reducing atmospheric CO_2 levels. The sheer scope of the issue is the addition of NaOH alone would not accomplish the goal of making oceans more basic. It would take a massive amount of base to fully neutralize the CO_2 that is beyond our capability. Additionally, the NaOH added
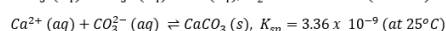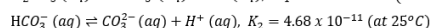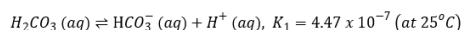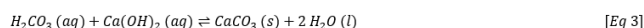
would quickly dissolve and raise the pH to very high levels in specific regions, which could cause severe environmental harm to local marine ecosystems. Thus, it is unfeasible to counteract ocean acidification through neutralization. In our experiments, we observed conversion of CO_2 into the fuel HCOOH in an electrolytic cell, but the identity of the products should be further investigated in studies with more precise laboratory equipment. Although this pathway of CO_2 management is effective in a small-scale setting, a greater number of trials must be done to determine its applicability to commercial industry, taking into account additional factors such as temperature, reaction duration, and type of base.

MATERIALS AND METHODS
CO2 Capture

The first part of the study was the capture process, which intended to investigate the relationship between NaOH concentration and precipitate formation, as well as increase in seawater pH. In this experiment, seawater was simulated with Perrier Carbonated Mineral Water (Perrier, Vergèze, France), which contains 68.2 mmol of CO_2 per 1 L of solution. The average salinity level of seawater is 34 parts per thousand (ppt) and the concentration of CO_2 is 2.3 mmol per 1 kg of water (14). Therefore, in order to replicate this, 4.59 g of table salt was dissolved in 135 mL of carbonated water. In total, 9.2 mmol of CO_2 was present. Additional variables such as temperature (25°C), pressure, and mineral content were kept constant across all conducted trials. $Ca(OH)_2$ was purchased from Lab Pro Inc. in solid powdered state. The chemical reaction illustrates a 1:1 molar ratio between CO_2 and $Ca(OH)_2$, so 0.682 g of $Ca(OH)_2$ was weighed with an electronic scale and dissolved in 400 mL of distilled water to create a saturated solution of 9.2 mmol. Distilled water was used instead of tap water in order to limit trace amounts of minerals, bacteria, contaminants, and other impurities, thus establishing it as an ideal control element. In six separate trials, the effect of initial pH was tested through varying concentrations of 10 mL of NaOH: 0.00 M, 0.04 M, 0.08 M, 0.12 M, 0.16 M, and 0.20 M. A starting solution of NaOH at 9.5625 M was purchased from Lab Pro Inc. Volumes of each intended molarity were diluted with distilled water until it reached a 500 mL aqueous solution.

The simulated seawater and NaOH (aq) were first combined in a glass beaker using a magnetic stirrer (100-2000 RPM) and spinbar (28 mm) on a hot plate at 270 oF. Three minutes later, the Ca(OH)2 solution was added as well. The beaker was allowed to sit on a table at room temperature for five hours in order to ensure the chemical reaction was driven to completion. The precipitation of $CaCO_3$ is given by the following reaction steps.

$$H_2CO_3\ (aq) + Ca(OH)_2\ (aq) \rightleftharpoons CaCO_3\ (s) + 2\,H_2O\ (l) \qquad [Eq\ 3]$$

$$H_2CO_3\ (aq) \rightleftharpoons HCO_3^-\ (aq) + H^+\ (aq),\ K_1 = 4.47\ x\ 10^{-7}\ (at\ 25°C)$$

$$HCO_3^-\ (aq) \rightleftharpoons CO_3^{2-}\ (aq) + H^+\ (aq),\ K_2 = 4.68\ x\ 10^{-11}\ (at\ 25°C)$$

$$Ca^{2+}\ (aq) + CO_3^{2-}\ (aq) \rightleftharpoons CaCO_3\ (s),\ K_{sp} = 3.36\ x\ 10^{-9}\ (at\ 25°C)$$
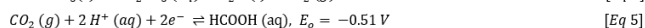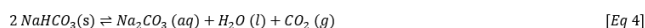
The resulting solution was filtered through a funnel using three stacked coffee filters in order to separate out the solid precipitate ($CaCO_3$). The precipitate was then transferred to a new beaker, air-dried, and massed. Additionally, using a water hydroponics digital pH meter, the pH of the seawater before and after the reaction were both measured to determine the

relative quantity of CO_2 removed.

Electrochemical Conversion

For the final conversion process, a one M solution of $NaHCO_3$ (sodium bicarbonate, simulated using baking soda) was transformed into the product HCOOH in a water electrolyzer unit through the following reaction steps.

$$2\,NaHCO_3(s) \rightleftharpoons Na_2CO_3\ (aq) + H_2O\ (l) + CO_2\ (g) \qquad [Eq\ 4]$$

$$CO_2\ (g) + 2\,H^+\ (aq) + 2e^- \rightleftharpoons HCOOH\ (aq),\ E_o = -0.51\ V \qquad [Eq\ 5]$$

A CO_2-based electrolyte bath was set up with commercial electrodes and Sn as the catalyst. The CO_2 chemically bonds to the surface of the metal catalyst and reacts with two H+ ions to form HCOOH, which can then be developed for commercial industrial use. Varying voltage potentials were then applied using a 30V, 50A adjustable DC bench linear power supply with alligator leads. The current density was measured, its value corresponding to the rate of reaction at the electrode surface.

REFERENCES
1. "CO_2 and Greenhouse Gas Emissions." *Our World in Data*. www.ourworldindata.org/co2-emissions. Accessed 28 June 2021.
2. "Ocean Acidification." *National Oceanic and Atmospheric Administration*.www.noaa.gov/education/resource-collections/ocean-coasts/ocean-acidification. Accessed 28 June 2021.
3. "What Is Ocean Acidification & Why Does It Matter?" *Columbia Climate School*. www.news.climate.columbia. edu/2015/12/09/what-is-ocean-acidification-why-does-it-matter/. Accessed 30 June 2021.
4. Kroeker, Kristy J., *et al.* "Impacts of ocean acidification on marine organisms: quantifying sensitivities and interaction with warming." *Global Change Biology*, vol. 19, no. 6, April 2013, doi.org/10.1111/gcb.12179.
5. Mangi, Stephen C., *et al.* "The economic impacts of ocean acidification on shellfish fisheries and aquaculture in the United Kingdom." *Environmental Science & Policy*, vol. 86, August 2018, doi.org/10.1016/j.envsci.2018.05.008.
6. Wuebbles, D.J., *et al.* "Climate Science Special Report." *Fourth National Climate Assessment*, vol. 1, US Global Change Research Program, 2017, doi:10.7930/J0J964J6.
7. La Plante, Erika C., *et al.* "Saline Water-Based Mineralization Pathway for Gigatonne-Scale CO2 Management." *ACS Sustainable Chem. Eng*, vol. 9, no. 3, January 2021, doi.org/10.1021/acssuschemeng.0c08561.
8. "How Much CO_2 Can The Oceans Take Up?" *The Keeling Curve UC San Diego.* www.keelingcurve.ucsd. edu/2013/07/03/how-much-co2-can-the-oceans-take-up/. Accessed 26 June 2021.

9. "Formic acid could fuel cars to mitigate climate change." *Sustainability Times*. www.sustainability-times.com/low-carbon-energy/formic-acid-could-fuel-cars-in-a-green-way/. Accessed 3 July 2021.

10. Liang, Shuyu, *et al.* "Electrolytic cell design for electrochemical CO_2 reduction." *Journal of CO_2 Utilization*, vol. 35, Jan. 2020, doi.org/10.1016/j.jcou.2019.09.007.

11. Zhao, Chenchen and Jianlong Wang. "Electrochemical reduction of CO_2 to formate in aqueous solution using electro-deposited Sn catalysts." *Chemical Engineering Journal*, vol. 293, June 2016, doi.org/10.1016/j.cej.2016.02.084.

12. Al-Tamreh, Shaima A., *et al.* "Electroreduction of Carbon Dioxide into Formate: A Comprehensive Review." *ChemElectrroChem*, vol. 8, no. 17, June 2021, doi.org/10.1002/celc.202100438.

13. Chang, Ribooga, *et al.* "Calcium Carbonate Precipitation for CO_2 Storage and Utilization: A Review of the Carbonate Crystallization and Polymorphism." *Frontiers in Energy Research*, July 2017, doi.org/10.3389/fenrg.2017.00017.

14. "Carbon Dioxide, Dissolved (Ocean)." *SOEST Hawaii*. www.soest.hawaii.edu/oceanography/faculty/zeebe_files/Publications/ZeebeWolfEnclp07.pdf. Accessed 14 July 2021.