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# Extraction of Carbon Dioxide from Seawater by an Electrochemical Acidification Cell Part I—Initial Feasibility Studies

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An electrochemical acidification cell is developed and tested as a method for extracting large quantities of carbon dioxide from seawater for use as a feedstock for jet-fuel synthesis at sea. The electrolytic regeneration of cation exchange resin was demonstrated, allowing simultaneous and continuous ion exchange and regeneration to occur within the cell along with control of the seawater pH. The $CO_2$ in the seawater was readily removed at pHs of less than 6.0. In addition, the cell produced a portion of the hydrogen needed for jet-fuel synthesis without additional energy penalties.

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# EXTRACTION OF CARBON DIOXIDE FROM SEAWATER BY AN ELECTROCHEMICAL ACIDIFICATION CELL PART I—INITIAL FEASIBILITY STUDIES

## 1.0 BACKGROUND

The feasibility of producing jet fuel at sea to support carrier flight operations is of interest. In-theater, synthetic fuel production is a "game changing" proposition that will offer the Navy significant logistical and operational advantages by reducing dependence on increasingly expensive fossil fuels and by reducing fuel logistic tails and their vulnerabilities resulting from unprotected fuel delivery at sea. The Navy has proposed moving to a common fuel JP5, throughout its operations [1]. However this has proven to be impractical due to the increase cost of the fuel and its limited availability. If the Navy does move to a single fuel this would simplify any future shipboard production of fuel. In addition, a ship's ability to produce any significant fraction of the battle group's fuel for operations would increase the Navy's operational flexibility and time on station by reducing the mean time between refueling.

Technologies currently exist to synthesize hydrocarbon fuel on land, given sufficient primary energy resources such as coal [2]. However, these technologies are not $CO_2$ neutral, and they are not practical for sea-based operation. Extracting carbon dioxide from seawater is part of a larger project to create liquid hydrocarbon fuel at sea [3-10]. $CO_2$ as a carbon feedstock could be catalytically reacted with hydrogen to form diesel and/or jet fuel. The hydrogen could be produced through commercial off the shelf conventional electrolysis equipment, and the electrical energy for this process would be derived through nuclear power or Ocean Thermal Energy Conversion (OTEC) [11-12]. This synthetic fuel production process could provide an alternative energy source to fossil fuels that would be directly intended to benefit the U.S. Navy. In 2008 the U.S. Navy's fuel procurement cost (purchase and delivery) was in excess of $5 billion [13]. Since this synthetic fuel process is intended for use by the U.S. Navy this process is envisioned as being performed on a sea-based platform.

## 2.0 INTRODUCTION

Practical, efficient, and economical methods of extracting large quantities of $CO_2$ from seawater must be developed before a sea-based synthetic fuel process that combines hydrogen produced by nuclear power or solar OTEC with $CO_2$ to make jet fuel can be envisioned [3-10]. The ocean's pH is kept relatively constant at approximately 7.8 by a complex carbonate buffer system. The equations below are the chemistry (eq. 1-5), charge balance (eq. 6), mass balance (eq. 7) and equilibrium equations (eq. 8-11) involved:

Chemistry: $\qquad CO_2 \text{ (g)} \rightleftarrows CO_2 \text{ (aq)}$ $\qquad\qquad$ (1)

$\qquad\qquad\qquad CO_2 \text{ (aq)} + H_2O \rightleftarrows H_2CO_3 \text{ (aq)}$ $\qquad\qquad$ (2)

$\qquad\qquad\qquad H_2CO_3 \text{ (aq)} \rightleftarrows H^+ + HCO_3^- \text{ (aq)}$ $\qquad\qquad$ (3)

$$HCO_3^- \text{ (aq)} \rightleftarrows H^+ + CO_3^{2-} \text{ (aq)} \qquad (4)$$

$$H_2O \rightleftarrows H^+ + OH^- \qquad (5)$$

Charge Balance: $\qquad 3[H^+] = [CO_3^{2-}] + [HCO_3^-] \qquad (6)$

Carbonate Mass Balance: $\qquad F_{H_2CO_3} = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3] \qquad (7)$

Equilibrium Equations at 25 °C: $\qquad K_{CO_2} = [CO_2(aq)]/P(CO_2) = 3.20 \times 10^{-2} \qquad (8)$

$$K_1 = [H^+][HCO_3^-]/[H_2CO_3] = 4.47 \times 10^{-7} \qquad (9)$$

$$K_2 = [H^+][CO_3^{2-}]/[HCO_3^-] = 4.69 \times 10^{-11} \qquad (10)$$

$$K_w = [H^+] + [OH^-] = 10^{-14} \qquad (11)$$

Where $CO_3^{2-}$ is carbonate ion, $CO_2$ is carbon dioxide, $H_2CO_3$ is carbonic acid, $H^+$ is hydrogen ion, $HCO_3^-$ is bicarbonate ion, and $OH^-$ is hydroxyl ion. $F_{H_2CO_3}$ represents mass balance on all species containing $CO_3^{2-}$ in units of mol $L^{-1}$ and P is the is the pressure in the equilibrium equation 8.

Using carbonate mass balance and acid equilibrium expressions, the fractional amounts of carbonate species as a function of $[H^+]$ are:

$$\alpha_{H_2CO_3} = [H^+]^2/([H^+]^2 + [H^+] K_1 + K_1K_2) \qquad (12)$$

$$\alpha_{HCO_3^-} = [H^+]K_1/([H^+]^2 + [H^+] K_1 + K_1K_2) \qquad (13)$$

$$\alpha_{CO_3^-} = K_1K_2/([H^+]^2 + [H^+]K_1 + K_1K_2) \qquad (14)$$

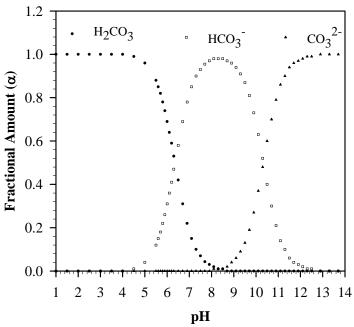The total carbonate can be expressed as a function of pH in Figure 1:

**Figure 1: Total Carbonate Expressed as a Function of pH**

By examining Figure 1, the fractional amounts of carbonate species at pH of 7.8 are $\alpha_{H2CO3} = 0.04$, $\alpha_{HCO3^-} = 0.96$, and $\alpha_{CO3^-} = 0.0$ indicating that 96 % of the carbon in the oceans is in the form of $HCO_3^-$. At pH of 4.5, it shows that 99 % of all carbonate species exist as $H_2CO_3$. $CO_2$ dissolved in water is in equilibrium with $H_2CO_3$ as shown in equation 15 as:

$$CO_2 + H_2O = H_2CO_3 \tag{15}$$

The hydration equilibrium constant is $1.70 \times 10^{-3}$. This indicates that $H_2CO_3$ is not stable and gaseous $CO_2$ readily dissociates at pH of 4.5, allowing $CO_2$ to be easily removed by degassing. In order to convert $HCO_3^-$ to $H_2CO_3$, the pH of seawater must be lowered.

A detailed composition of seawater shows a carbon (C) concentration of 28 ppm (~100 mg/L as $CO_2$). Assuming that C exists as $HCO_3^-$, the $HCO_3^-$ concentration in seawater will be approximately 142 ppm (0.0023 M), therefore approximately 23 mL of 0.100 M hydrochloric acid (HCl) acid is required per liter of seawater where $Cl^-$ is chloride ion.

$$HCl + HCO_3^- \rightarrow H_2CO_3 + Cl^- \tag{16}$$
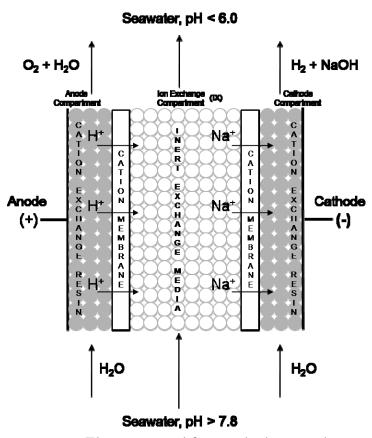
Johnson et al. demonstrated this concept when they showed that $CO_2$ existed only in the dissolved gas form when the pH of seawater was decreased to 6 or less [14]. Based on these principles, Hardy et al. investigated the use of simple strong cation exchange resin systems to increase the rate and yield of carbon dioxide recovery from seawater [3]. They successfully utilized the ion exchange material to acidify the seawater below pH 6. However, the volume of water per unit weight of resin required to regenerate the resin was much larger than the volume of $CO_2$ recovered, and potentially larger than the volume of fuel produced from the $CO_2$. As a result the approach was deemed impractical for a sea-based application [3]. Thus as one further

avenue to exploit the pH as a means to recover carbon from the sea, an electrochemical acidification cell that is able to decompose water into $H^+$, $OH^-$, hydrogen gas ($H_2$), and oxygen gas ($O_2$) by means of electrical energy has been developed and tested. The effects of acidification cell configuration, seawater composition, flow rate, and current on seawater pH are discussed. These data are used to determine the feasibility of this approach for a carbon capture process.

The approach described within is considerably different than traditional electrolysis methods that are specifically tailored toward the production of hydrogen and oxygen from seawater and or fresh water. Most modern military submarines generate their breathing oxygen from the electrolysis of fresh water [15]. The difficulty with current seawater electrolysis technology for hydrogen production is the formation of chlorine gas and thus electrodes are modified such that only oxygen is evolved at the anode [16].

## 3.0 TEST DESCRIPTION

3.1 Electrochemical Acidification Cell

Seawater, pH < 6.0

$O_2 + H_2O$                    $H_2 + NaOH$

Anode Compartment    Ion Exchange Compartment (IX)    Cathode Compartment

CATION EXCHANGE RESIN    $H^+$    CATION MEMBRANE    INERT EXCHANGE MEDIA    Na⁺    CATION MEMBRANE    CATION EXCHANGE RESIN

Anode (+)    $H^+$    Na⁺    Cathode (-)

$H^+$    Na⁺

$H_2O$    $H_2O$

Seawater, pH > 7.8

← Electrons travel from cathode to anode
Positive ions travel from anode to cathode→

**Figure 2. Electrochemical Acidification Cell**

The major components of an acidification cell include a central ion exchange (IX) compartment, electrode compartments (cathode and anode) and cation-permeable membranes which separate the three compartments.  A cation-permeable membrane is a cross-linked polymer backbone with sulfonic acid groups attached to it.  The acid functionality provides discrete channels for cations to migrate through the polymer matrix while blocking the passage of anions.  Figure 2 shows a typical three compartment cell configuration.

Two different types of ion exchange media, strong cation exchange resin (IRA-120) from Rohm & Haas and inert ceramic particles, were tested in the IX compartment to evaluate and determine its effects on the exchange of $Na^+$ for $H^+$ ions in the cell.  This will be significant in the overall efficiency of the cell. These media also served as a support structure for the membranes.  In addition Figure 2 shows that the electrode compartments contained strong cation exchange resin (IRA-120).

The acidification cell in Figure 2 uses small quantities of electricity to exchange sodium ions for hydrogen ions in a central stream that is flowing adjacent to two cation exchange membranes. Seawater is passed through the center compartment of the three compartment cell.  Sodium ions are transferred through the membrane closest to the cathode and removed from the seawater by means of direct current (DC) voltage.  These sodium ions are replaced by hydrogen ions as the current drives the ions through the membrane closest to the anode to acidify the seawater.

In the cell, the anolyte is the water fed to the anode compartment.  At the anode $H^+$ is generated and it must migrate from the surface of the anode, through the cation-permeable membrane, and into the IX compartment where it can replace $Na^+$.  Therefore the anolyte must be as diluted as possible such that $H^+$ are in excess and do not compete with any other cations.  Water with a conductivity of less than 20 µS/cm, such as reverse osmosis (RO) permeate, is required.  In this evaluation, deionized water was used as the anolyte, so the effect of RO permeate as a catholyte cannot be evaluated during this feasibility test.

The catholyte is the water fed to the cathode compartment and it must be free from hardness ions calcium ($Ca^{+2}$) and magnesium ($Mg^{+2}$).  The pH in the cathode compartment is high enough to precipitate these hardness ions.  Therefore, a total hardness concentration of less than 50 ppm, such as RO permeate, is required.  In this evaluation, deionized water will be used as the catholyte, so the effect of RO permeate cannot be evaluated during this feasibility test.

In this test series two different acidification cells were evaluated; Nalco and Ionpure.  Tables 1 and 2 provide a detailed description of each cell's electrical and flow rate specifications along with the materials used in the cell configurations.  The anode used in the Nalco cell is a dimensionally stable anode (DSA)  (mixed precious metal oxide coating on titanium), where the Ionpure cell uses a platinum plated titanium anode.  This feasibility test will determine the flow rate to current ratio required to lower seawater pH to a target level.  This information will be useful for the future design of an acidification cell, since electrode performance and operating life is based on current density (mA cm$^{-2}$).  In addition to having different anode materials, each cell contains a different type of cation-permeable membrane.  The Nalco cell contains Sybron's MC-3470 reinforced/casted cation permeable membrane, while the Ionpure cell contains a

polyethylene extruded cation permeable membrane.  Membrane performance cannot be evaluated during this feasibility test, since its performance and operating life is based on current density and level of organic compounds contained in the seawater (not possible with synthetic seawater).

Table 1.  Nalco Cell Configured as an Electrochemical Acidification Cell

| Dimensions | |
| --- | --- |
| Approximate Overall Cell Dimension | 14.0 cm x 36.5 cm x 6.0 cm |
| IX Compartment Width | 5.1 cm |
| IX Compartment Height | 30.1 cm |
| IX Compartment Thickness | 1.2 cm |
| IX Compartment Volume | 184.2 cm$^3$ |
| Membranes Active Area | 153.5 cm$^2$ |
| Electrode Compartment Volume | 98.4 cm$^3$ |
| **Electrical Specification** | |
| Electrode Active Area | 153.5 cm$^2$ |
| Max. Current Density | 100 A m$^{-2}$ |
| **Flow Specification** | |
| Max. Flow Rate | 20 cm$^3$ s$^{-1}$ |
| Max. Electrolyte Flow Rate | 10 cm$^3$ s$^{-1}$ |
| Max. Operating Temperature | 60 °C |
| Max. Operating Pressure | 350 kPa |
| **Materials** | |
| Anode | Dimensionally Stable Anode (DSA-600) |
| Cathode | 316L Stainless Steel |
| Membrane | Sybron Cation-Permeable Membrane |
| Molded Frame and End Block | Acrylonitrile Butadiene Styrene (ABS) |

Table 2.  Ionpure Cell Configured as an Electrochemical Acidification Cell

| Dimensions | |
|---|---|
| Approximate Overall Cell Dimension | 33 cm x 61 cm x 8 cm |
| IX Compartment Width | 14 cm |
| IX Compartment Height | 35.5 cm |
| IX Compartment Thickness | 0.9 cm |
| IX Compartment Volume | 429 cm$^3$ |
| Membranes Active Area | 497 cm$^2$ |
| Electrode Compartment Volume | 214 cm$^3$ |
| **Electrical Specifications** | |
| Electrode Active Area | 497 cm$^2$ |
| Max. Current Density | 400 A m$^{-2}$ |
| **Flow Specifications** | |
| Max. Flow Rate | 35 cm$^3$ s$^{-1}$ |
| Max. Electrolyte Flow Rate | 35 cm$^3$ s$^{-1}$ |
| Max. Operating Temperature | 60 °C |
| Max. Operating Pressure | 350 kPa |
| **Materials** | |
| Anode | (Platonized Titanium) |
| Cathode | 316L Stainless Steel |
| Membrane | Ionpure Cation-Permeable Membrane |
| Molded Frame and End Block | Polyethylene (PE) |

3.2  Electrochemical Acidification Tests

Figure 3 is a schematic that describes the acidification experimental set-up.  Seawater was passed upwardly through the IX compartment.  Deionized water at a pH of approximately 6.7 was passed upwardly through the anode compartment and then upwardly through the cathode compartment (in series).  A controlled current was applied to the anode and cathode in order to lower the pH of the seawater to a target level.  This was a single pass system, so once a volume of seawater and deionized water passed through the cell; it was not utilized again in the test.
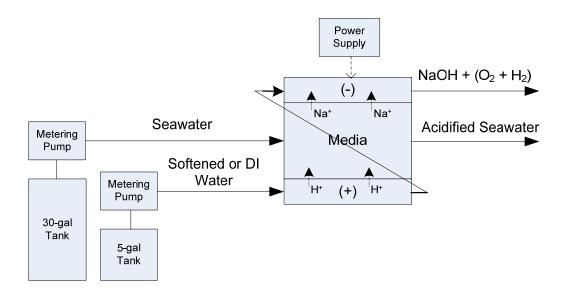
**Figure 3. Schematic Showing the Acidification Experimental Layout**

Five different types of seawater were evaluated in this test series. Four of these types were synthetic formulations (designated as IO1, IO2, IO3, IO4) created from instant ocean seawater while the other was actual seawater came from our NRL Key West Florida laboratory facility (KW). The synthetic formulations were prepared at least 16 hours prior to usage to allow the buffer salts to reach equilibrium. Below is the concentrations and measured pH of the seawater solutions. The pH of the solutions varied as a result of equilibration with $CO_2$ gas in the atmosphere. These pH changes had no effect on the overall performance of the acidification cell. All pH measurements were conducted with a standardized Fisher combination glass electrode. Carbon dioxide content of solutions were measured by a UIC Coulometric system (UIC Inc, Joliet, IL 60436) [15].

IO 1 - Synthetic seawater was prepared by dissolving 41.1 g $L^{-1}$ of Instant Ocean Sea Salt in deionized water at a total volume of 100 liters. The pH of the synthetic seawater was 9.1 ± 0.5. The $CO_2$ content was not measured.

IO 2 - Synthetic seawater was prepared by dissolving 35 g $L^{-1}$ of Instant Ocean Sea Salt (in deionized water at a total volume of 140 liters. The pH of the synthetic seawater was 8.4 ± 0.2. The $CO_2$ content was not measured.

IO 3 – Synthetic seawater, using Instant Ocean Sea Salt at 35 g $L^{-1}$, was supplemented with 90 ppm of sodium bicarbonate and diluted with deionized water to a total volume of 140 liters. The pH of the synthetic seawater was 8.2. The $CO_2$ content was measured to be approximately 100 ppm.

<u>IO 4</u> – Synthetic seawater, using Instant Ocean Sea Salt at 35 g L$^{-1}$, was supplemented with 90 ppm of sodium bicarbonate and diluted with deionized water to a total volume of 140 liters, and pH adjusted to 7.6 using hydrochloric acid (HCl); approximately 20 mLs of diluted HCl (5 mL of concentrated HCl diluted to 50 mL) was added to 100 liters of synthetic seawater. The $CO_2$ content was measured to be approximately 100 ppm.

<u>KW</u> – Actual Seawater from Naval Research Laboratory Key West, Florida. The pH was 7.6 ± 0.2 and the $CO_2$ content was measured to be approximately 100 ppm. Only seven liters was available.

Degassing measurements were made on selective samples during the course of the experiment. For each measurement carbon dioxide was degassed from solution using a Brinkmann Roto-Evaporator. A 20 mL sample was placed in a 1000 mL round bottom flask and rotated at an rpm setting of 8 for five minutes. A water aspiration provided a vacuum of approximately 15 mm Hg.

## 4.0 ELECTROCHEMCAL ACIDIFICATION CELL REACTIONS

Figure 2 shows an acidification cell exchanging $Na^+$ for $H^+$ in a stream that is flowing adjacent to two cation-permeable membranes. A small amount of electricity facilitates this exchange. Depicting seawater by sodium chloride (NaCl) and acidified seawater by HCl, the reactions within an electrochemical acidification cell are as follows:

$$\text{Anode:} \qquad 2H_2O \rightarrow 4H^+ + O_2 + 4e^- \qquad (17)$$

$$\text{IX:} \qquad 4|NaCl|_{Seawater} + 4H^+ \rightarrow 4\,Na^+ + 4|HCl|_{Acidic\ Seawater} \qquad (18)$$

$$\text{Cathode:} \qquad 4H_2O + 4Na^+ + 4e^- \rightarrow 4NaOH + 2H_2 \qquad (19)$$

$$\text{Overall:} \qquad 6H_2O + 4NaCl \rightarrow 4|HCl|_{IX} + 4|NaOH| + 2|H_2|_{Cathode} + |O_2|_{Anode} \qquad (20)$$

The amount of $H^+$ generated is proportional to the applied electrical current, which follows Faraday's constant. Faraday's constant is defined as the amount of electricity associated with one mole of unit charge or electron, having the value 96,487 ampere-second/equivalent.

For the anode reaction, 96,487 A sec will produce ¼ mole $O_2$ gas and 1 mole $H^+$ and for the cathode reaction, 96,487 A sec will produce ½ mole $H_2$ gas and 1 mole $OH^-$. This allows the amount of $H^+$, $OH^-$, $H_2$, and $O_2$ produced per amp/second of current passed through the electrodes to be determined:

<u>Anode Reaction</u>

$$\left(\frac{1/4 \text{ mole O}_2}{96{,}487 \text{ A-sec}}\right)\left(\frac{60 \text{ sec}}{\text{min}}\right) = 0.000155 \frac{\text{mole O}_2}{\text{A-min}} \qquad (21)$$

$$\left(\frac{1 \text{ mole H}^+}{96{,}487 \text{ A-sec}}\right)\left(\frac{60 \text{ sec}}{\text{min}}\right) = 0.000622 \frac{\text{mole H}^+}{\text{A-min}} \qquad (22)$$

<u>Cathode Reaction</u>

$$\left(\frac{1/2 \text{ mole H}_2}{96{,}487 \text{ A-sec}}\right)\left(\frac{60 \text{ sec}}{\text{min}}\right) = 0.000311 \frac{\text{mole H}_2}{\text{A-min}} \qquad (23)$$

$$\left(\frac{1 \text{ mole OH}^-}{96{,}487 \text{ A-sec}}\right)\left(\frac{60 \text{ sec}}{\text{min}}\right) = 0.000622 \frac{\text{mole OH}^-}{\text{A-min}} \qquad (24)$$

Therefore, seawater with a $HCO_3^-$ concentration of 142 ppm (0.0023 M) and flow rate of 1 liter per minute, a theoretical applied current of 3.75 A will be required to lower the pH to less than 6.0 and convert $HCO_3^-$ to $H_2CO_3$.

$$\frac{\left(\dfrac{0.0023 \text{ mole HCO}_3^-}{\text{Liter}}\right)\left(\dfrac{1 \text{ Liter}}{\text{min}}\right)}{\left(\dfrac{0.000622 \text{ mole H}^+}{\text{A-min}}\right)} = 3.75 \text{ A} \qquad (25)$$

Current efficiency can be defined as the ratio of the theoretical minimum current predicted by Faraday's law to the actual current applied to the electrodes of the acidification cell. In actuality, current efficiencies are never 100 % and can range from 30 to 95 % based on the conductivity of the liquid being treated; the higher the conductivity, the greater the current efficiency. It is estimated that current efficiency for seawater is on the order of 70 to 90 %. Therefore,

$$\text{Acutal Current} = \left(\frac{\text{Theoretical Current}}{\text{Current Efficiency}}\right) = \left(\frac{3.75 \text{ A}}{80 \%}\right) = 4.69 \text{ A} \qquad (26)$$

The theoretical amount of $CO_2$ that can be removed from the acidified seawater is 0.0023 moles per liter. Removal efficiency can be defined as the ratio of the theoretical amount of $CO_2$ removed to the actual amount of $CO_2$ removed in the acidified seawater. Removal efficiencies are never 100 % and can range from 50 to 95 % based on various unit operating requirements. The overall removal of $CO_2$ is conservatively estimated to be approximately 50 %.

$$\text{Actual Removal} = \left(\frac{\text{Theoretical Removal}}{\text{Removal Efficiency}}\right) = \left(\frac{0.0023 \text{ mole/min}}{50 \%}\right) = 0.0046 \frac{\text{mole CO}_2}{\text{min}} \qquad (27)$$

The amount of $H_2$ gas generated at 4.75 A is

$$(\frac{1/2\,\text{mole}\,H_2}{96{,}487\,A\text{-}\sec})(\frac{60\,\sec}{\min})(\,4.75A) = 0.0015\frac{\text{mole}\,H_2}{\min} \qquad (28)$$

Under these theoretical conditions, the molar ratio of $H_2$ and $CO_2$ is 0.32. Increasing the current increases the molar ratio of hydrogen to carbon dioxide with no effect on the operation of the acidification cell. $H^+$ generated will either exchange with $Na^+$ in the seawater to further lower its pH or migrate through the IX compartment and into the cathode compartment where it will combine with $OH^-$ to form water.

## 5.0 RESULTS AND DISCUSSION

In the first test of the feasibility studies, the Nalco cell (Table 1) was configured such that strong acid cation exchange resin was used to fill both the ion exchange compartment (IX) and the electrode compartments (Figure 2). IO-1 seawater was used as the influent, and passed through the IX compartment at 140 ml/min for 165 minutes. The rate of dionized water through the electrode compartments was increased to a final flow rate of 140 mL/min. The results summarized in Table 3 show that when 3 amps of current where applied to the cell, the pH of the effluent seawater was between 2.08 and 2.15. As the current was decreased from 3 to 0.25 amps, the pH of the effluent seawater was increased to 5.88. These results demonstrate that the pH of the effluent seawater can be lowered using the acidification cell as it is configured and it is proportional to the applied current. The results also demonstrate the electrolytic regeneration of the cation exchange resin. The flow rate to current ratio when the seawater pH was 5.88 is estimated to be 560 by the following data:

Table 3 Data:        140 mL/min/0.25 amps = 560

This ratio is higher than the theoretical ratio of 267 calculated for the same conditions as described in equation 25 as:

1000 mL/min/3.75 amps = 140 mL/min/X

X= 0.525 Amps

Theoretical Ratio:     140 mL/min/0.525 amps = 267

This indicates that the $HCO_3^-$ levels in the IO-1 synthetic formulation may not be at the correct concentration, even though the pH was high.

The recovery was at 50% and not lowered in this experiment. The term "recovery" is used to define the ratio of product quantity (influent seawater flow rate, Table 3) over the total feed quantity to the cell (influent seawater flow rate and influent dionized flow rate, Table 3) as a percent. This is critical since the water required in the electrode compartments must be dilute and free from hardness ions. This type of water must be treated by a filtration process such as reverse osmosis. A high recovery will allow the size of the filtration unit along with the energy requirements for the unit to be minimized.

Table 3.  Test 1: Acidification of IO-1 seawater at 140 mL/min

| Time, min | Amp/Volt | Influent Seawater Flow Rate, mL min$^{-1}$ | Influent DI Flow Rate, mL min$^{-1}$ | Effluent Acidified Seawater pH | Effluent DI Cathode pH |
|---|---|---|---|---|---|
| 15 | 3.0 / 9.0 | 150 | 80 | 2.08 | 12.69 |
| 30 | 3.0 / 10.0 | 140 | 77 | - | - |
| 45 | 3.0 / 10.0 | 140 | 75 | 2.15 | 12.63 |
| 60 | 3.0 / 11.0 | 140 | 75 | 2.10 | 12.49 |
| 75 | 3.0 / 12.0 | 140 | 144 | - | - |
| 90 | 2.0 / 9.0 | 140 | 140 | 2.19 | 12.13 |
| 105 | 1.0 / 6.0 | 140 | 140 | 2.70 | 12.00 |
| 120 | 0.5 / 4.0 | 140 | 140 | 3.61 | 11.41 |
| 135 | 0.25 / 3.0 | 140 | 140 | 5.88 | 11.26 |
| 150 | 0.0 / 0.0 | 140 | 140 | - | - |
| 165 | 0.0 / 0.0 | 140 | 140 | 8.76 | 10.41 |

In the second test, a similar IO synthetic formulation was made (IO-2) and used to determine the effect that flow rate through the IX compartment had on the performance of the Nalco cell. Initially IO-2 was pumped at 900 mL/min before a flow of 860 mL/min was established and maintained after 90 minutes.  The results summarized in Table 4 establish that at higher flow rates the pH of the effluent seawater can be lowered using the acidification cell.  Higher influent seawater flow rates increase the percent recovery from 50% to 86%.  In addition the results suggest that the flow rate to current ratio was improved from 560 to 716 (860 mL/min/1.20 amps).

Table 4.  Test 2: Acidification of IO-2 seawater at 900 mL/min

| Time, min | Amp/Volt | Influent Seawater Flow Rate, mL min$^{-1}$ | Influent DI Flow Rate, mL min$^{-1}$ | Effluent Acidified Seawater pH | Effluent DI Cathode pH |
|---|---|---|---|---|---|
| 15 | 1.0 / 5.0 | 900 | 140 | 7.31 | 11.79 |
| 30 | 1.5 / 7.0 | 900 | 140 | 6.13 | 12.06 |
| 45 | 1.5 / 7.0 | 864 | 140 | 5.95 | 12.04 |
| 60 | 1.5 / 7.0 | 870 | 140 | 4.63 | 11.90 |
| 75 | 1.5 / 7.0 | 864 | 140 | 4.41 | 11.89 |
| 90 | 1.5 / 7.0 | 868 | 140 | 4.30 | 11.75 |
| 105 | 1.5 / 7.0 | 860 | 140 | 4.18 | 11.76 |
| 120 | 1.5 / 7.0 | 860 | 140 | 4.05 | 11.74 |
| 135 | 1.0 / 6.0 | 860 | 140 | 6.31 | 11.12 |
| 150 | 1.0 / 6.0 | 860 | 140 | 6.20 | 11.42 |
| 165 | 1.0 / 6.0 | 860 | 140 | 6.27 | 11.52 |
| 180 | 1.2 / 6.5 | 860 | 140 | 6.17 | 11.20 |

The third test examines the effects of replacing the strong cation exchange material in the IX compartment of the cell with inert ceramic particles. The affects of the ceramic media on the ion exchange efficiency of $Na^+$ for $H^+$ ions in the cell is determined in the results shown in Table 5.

Table 5.  Test 3: Acidification of IO-2 seawater at 680 mL/min using Inert Material in the
IX compartment

| Time, min | Amp/Volt | Influent Seawater Flow Rate, mL min$^{-1}$ | Influent DI Flow Rate, mL min$^{-1}$ | Effluent Acidified Seawater pH | Effluent DI Cathode pH |
|---|---|---|---|---|---|
| 15 | 1.0 / 8.0 | 680 | 140 | 8.29 | 11.88 |
| 30 | 1.0 / 8.0 | 680 | 140 | 8.48 | 11.88 |
| 45 | 1.0 / 8.0 | 680 | 140 | 8.28 | 11.87 |
| 60 | 1.0 / 8.0 | 680 | 140 | 7.13 | 11.87 |
| 75 | 1.0 / 8.0 | 680 | 140 | 6.62 | 11.90 |
| 90 | 1.0 / 8.0 | 680 | 140 | 6.10 | 11.88 |
| 105 | 1.0 / 8.0 | 680 | 140 | 5.51 | 11.88 |
| 120 | 1.0 / 8.0 | 680 | 140 | 4.22 | 11.52 |
| 135 | 1.0 / 8.0 | 680 | 140 | 6.46 | 11.25 |
| 150 | 0.8 / 6.0 | 680 | 140 | 6.30 | 11.33 |
| 165 | 0.9 / 6.5 | 680 | 140 | 5.87 | 11.36 |
| 180 | 0.9 / 7.0 | 680 | 140 | 5.83 | 11.42 |

At a flow rate of 680 mL/min to the IX compartment and an applied current of 1.0 amps, the pH of IO-2 is reduced from 8.29 to 6.3 in 150 minutes.  Since the pH of the IO-2 water can be lowered with the inert media in the IX compartment the process is considered to be an electrically driven membrane process.  The progressive decrease in the IO-2 pH indicates that the cation exchange resin in the anode compartment was regenerating.  Since the cation exchange resin in the anode compartment was in the sodium form during the start of the experiment, $H^+$ ions from the oxidation of water on the anode exchanged on the resin and released $Na^+$ ions. These $Na^+$ ions then migrated through the cation exchange membrane and into the IX compartment.  Breakthrough of $H^+$ ions into the IX compartment began at 60 minutes when the pH of the seawater began to decrease.  See Figure 1 for illustrative details.  The high and stable pH of the NaOH is a result of this.  In addition to the electrically driven membrane process, the flow rate to current ratio was further improved from 716 to 755 (680 mL/min/0.90 amps) at a recovery of 83%.

When the flow rates to the IX compartment and the electrode compartments were dropped (680 mL/min to 140 mL/min in the IX compartment) (120 mL/min to 18 to 10 mL/min) as shown in Table 6, there was an improvement in the flow rate to current ratio 1,207 (140 mL/min/0.116 amps).  In addition, the lower flow rates to the cell increased the recovery from 88 to 95%.

Table 6. Test 4: Acidification of IO-2 seawater at 140 mL/min using Inert Material in the IX compartment

| Time, min | Amp/Volt | Influent Seawater Flow Rate, mL min$^{-1}$ | Influent DI Flow Rate, mL min$^{-1}$ | Effluent Acidified Seawater pH | Effluent DI Cathode pH |
|---|---|---|---|---|---|
| 60 | 0.178 / 4.75 | 140 | 18 | 3.96 | 10.82 |
| 120 | 0.169 / 4.63 | 140 | 16 | 4.19 | 10.92 |
| 180 | 0.136 / 4.27 | 140 | 17 | 5.30 | 10.84 |
| 240 | 0.116 / 4.03 | 140 | 18 | 6.07 | 10.82 |
| 300 | 0.116 / 3.99 | 140 | 17 | 5.75 | 10.92 |
| 360 | 0.116 / 3.91 | 140 | 10 | 5.92 | 10.84 |
| 420 | 0.116 / 3.79 | 140 | 10 | 5.88 | 10.88 |

With the optimum cell configuration and flow rates established by previous experiments, Key West seawater was used in order to simulate sample conditions that would be encountered in an actual ocean process for sequestering $CO_2$. The results summarized in Table 7 show the flow rate to current ratio was significantly reduced to approximately 298 (140 mL/min / 0.47 amps).

Table 7. Test 5: Acidification of KW seawater at 140 mL/min using Inert Material in the IX compartment

| Time, min | Amp/Volt | Influent Seawater Flow Rate, mL min$^{-1}$ | Influent DI Flow Rate, mL min$^{-1}$ | Effluent Acidified Seawater pH | Effluent DI Cathode pH |
|---|---|---|---|---|---|
| 1 | 0.15 / 3.14 | 140 | 10 | 5.52 | - |
| 2 | 0.15 / 3.13 | 140 | 10 | 6.05 | - |
| 3 | 0.15 / 3.14 | 140 | 10 | 6.14 | - |
| 4 | 0.15 / 3.14 | 140 | 10 | 6.23 | - |
| 5 | 0.15 / 3.14 | 140 | 10 | 6.29 | |
| 6 | 0.17 / 3.21 | 140 | 10 | 6.35 | - |
| 7 | 0.17 / 3.23 | 140 | 10 | 6.35 | - |
| 9 | 0.19 / 3.37 | 140 | 10 | 6.42 | - |
| 11 | 0.21 / 3.45 | 140 | 10 | 6.42 | - |
| 13 | 0.26 / 3.61 | 140 | 10 | 6.37 | - |
| 15 | 0.31 / 3.84 | 140 | 10 | - | - |
| 17 | 0.40 / 4.06 | 140 | 10 | 6.20 | - |
| 19 | 0.47 / 4.33 | 140 | 10 | 6.09 | - |
| 21 | 0.47 / 4.34 | 140 | 10 | 6.04 | - |
| 23 | 0.47 / 4.33 | 140 | 10 | 5.97 | - |

This ratio is very similar to the theoretical ratio of 267, indicating the correct $HCO_3^-$ level, and the recovery was at 94 %. When the $CO_2$ content of the KW seawater was measured by coulometery, it was found to contain 4 times more alkalinity than measured in the IO-1 and IO-2

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seawater formulations.  This is clearly evident by the data in Table 7 which shows that it required 0.47 amps to decrease the pH of the Key West seawater from 7.60 to 5.97.  Previous acid titrations used to access the $CO_2$ concentration of the Key West seawater were consistent with the results of this example.  An average of 20 mLs of 2.00E-03 M of hydrochloric acid was required to reduce pH in a 20 mL sample of Key West seawater to 6.0.  This required 4.05E-05 moles of hydrogen ions.  Based on a flow rate of 140 mL/min and the use of Faraday's constant, 0.000622 mol $H^+$/A-min (equation 22), a current of 0.46 amps will generate 4.05E-05 moles of hydrogen ions.  This gives an indication that the current efficiency in the electrolytic cell was approximately 98 % (4.6/4.7).

In the sixth test of the series, a new IO formulation (IO-3) was made that had a similar alkalinity concentration as that found in KW.  However, the pH was 8.19 compared to the 7.67 measured for KW.  Table 8 shows that the amount of current required to reduce the pH of IO-3 from 8.19 to 6.0 was approximately three times higher than that seen in previous test.  The flow rate to current ratio was approximately 111 (140 mL $min^{-1}$ / 1.26 amps), which is lower than the theoretical ratio of 267.  The recovery was between 88 and 95 %.  The $CO_2$ content in IO-3 was found to be adequate so the low ratio may be associated with the acidification cell not operating long enough to reach equilibrium.

Table 8.  Test 6: Acidification of IO-3 seawater at 140 mL/min using Inert Material in the IX compartment

| Time, min | Amp/Volt | Influent Seawater Flow Rate, mL $min^{-1}$ | Influent DI Flow Rate, mL $min^{-1}$ | Effluent Acidified Seawater pH | Effluent DI Cathode pH |
|---|---|---|---|---|---|
| 15 | 0.46 / 4.58 | 140 | 10 | 6.52 | - |
| 30 | 0.48 / 4.89 | 138 | 9 | 6.42 | - |
| 45 | 0.49 / 4.71 | 140 | 18 | 6.48 | - |
| 60 | 0.49 / 4.69 | 138 | 9 | 6.78 | - |
| 75 | 0.51 / 4.79 | 140 | 9 | 6.65 | |
| 90 | 0.65 / 5.31 | 139 | 8 | 6.48 | - |
| 105 | 0.72 / 5.66 | 140 | 18 | 6.36 | - |
| 120 | 0.99 / 6.74 | 140 | 18 | 6.24 | - |
| 135 | 1.12 / 7.27 | 140 | 19 | 6.10 | - |
| 150 | 1.26 / 7.90 | 140 | 19 | 5.94 | - |
| 165 | 1.44 / 8.46 | 140 | 19 | 5.78 | - |
| 180 | 1.66 / 9.75 | 140 | 18 | 5.57 | - |
| 195 | 1.99 / 12.17 | 140 | 18 | 5.14 | - |
| 225 | 1.99 / 12.06 | 140 | 9 | 5.03 | - |
| 255 | 1.31 / 9.77 | 140 | 9 | 5.86 | - |

A new IO formulation for Test 7 was made in an effort to create a synthetic system that had a similar pH and alkalinity to KW.  When IO-4 was used to challenge the acidification cell, the results shown in Table 8 indicate that the amount of current required to reduce the pH to 6.0 was

approximately two times higher (0.47 vs 0.89 amps).  The flow rate to current ratio was approximately 157 (140 mL/min / 0.89 amps), which is lower than the theoretical ratio of 267. The recovery at these flow rates was between 88 and 95 %.  The $CO_2$ content in IO-4 was found to be adequate so the low ratio may be associated with the acidification cell not operating long enough to reach equilibrium.

Table 9.  Test 7: Acidification of IO-4 seawater at 140 mL/min using Inert Material in the IX compartment

| Time, min | Amp/Volt | Influent Seawater Flow Rate, mL min$^{-1}$ | Influent DI Flow Rate, mL min$^{-1}$ | Effluent Acidified Seawater pH | Effluent DI Cathode pH |
|---|---|---|---|---|---|
| 15 | 1.33 / 12.23 | 140 | 9 | 3.42 | - |
| 30 | 0.97 / 10.51 | 140 | 9 | 5.57 | - |
| 45 | 0.88 / 9.89 | 140 | 9 | 6.11 | - |
| 75 | 0.89 / 10.20 | 140 | 9 | 6.03 | - |
| 105 | 0.89 / 10.50 | 140 | 9 | 6.09 | |
| 135 | 0.89 / 10.88 | 140 | 19 | 6.19 | - |
| 210 | 1.51 / 13.79 | 140 | 19 | 2.76 | - |
| 255 | 1.15 / 12.43 | 140 | 19 | 4.42 | - |

The feasibility of scaling this process was the objective of test 8 (Table 10) in the test series.  The larger Ionpure cell (Table 2) was configured similarly to the Nalco cell used in Tests (3-7).  IO-4 was used to challenge the cell at a flow rate of 1050 mL/min to the IX compartment.  From Table 10 the amount of current required to reduce the pH from 7.6 to 4.5 was approximately 4.87 amps.  The flow rate to current ratio was approximately 216 (1050 mL min$^{-1}$ / 4.87 amps).  This ratio is lower than the theoretical ratio of 267.  The recovery was 90 %.  Since the $CO_2$ content in IO-4, was similar to that measured in KW, the low ratio may be associated with the acidification cell not operating long enough to reach equilibrium.

Table 10.  Test 8: Acidification of IO-4 seawater at 1050 mL/min using Inert Material in the IX compartment of the Ionpure Cell

| Time, min | Amp/Volt | Influent Seawater Flow Rate, mL min$^{-1}$ | Influent DI Flow Rate, mL min$^{-1}$ | Effluent Acidified Seawater pH | Effluent DI Cathode pH |
|---|---|---|---|---|---|
| 20 | 3.51 / 5.62 | 1050 | 116 | 7.18 | - |
| 40 | 4.49 / 6.74 | 1050 | 118 | 6.82 | - |
| 60 | 5.54 / 7.52 | 1050 | 118 | 6.24 | - |
| 80 | 6.53 / 8.40 | 1050 | 114 | 4.23 | - |
| 100 | 6.24 / 8.24 | 1050 | 114 | 3.44 | |
| 120 | 5.02 / 7.42 | 1050 | 116 | 4.75 | - |
| 140 | 4.75 / 7.24 | 1050 | 116 | 4.21 | - |

The Ionpure cell was re-configured in test 9 (Table 11) such that no material was used in IX compartment of the cell. Table 11 shows that the results were consistent with the results in test 8 (Table 10) during the first 100 minutes of operation which further indicates that this process is an electrically driven membrane process, whereas the media contained in the IX compartment has no effect on the acidification of the seawater. After 100 minutes of operation, voltage and flow rate irregularities occurred indicating internal disruption due to non supported membranes. The pH began to increase and flow rate decrease in the IX compartment while the flow rate increased and pH decreased in the electrode compartments, indicating a gross leak between compartments.

Towards the end of this test 9 (Table 11), a crude electrode gas ($H_2$ and $O_2$) capture experiment was performed, but both gasses were captured together due to a common electrode compartment inlet and outlet. The combined gas captured was approximately 10 mL/min per amp. This is close to theoretical according to Faraday's law which indicated 10.5 ml/min (7. 0 mL/min $H_2$ + 3.5 mL/min $O_2$) per amp at the standard conditions of temperature and pressure. The acidification cell that will be used in future tests will have separate anode and cathode inlets and outlets so that each gas is separate and its volume will be better quantified.

Table 11. Test 9: Acidification of IO-4 seawater at 1050 mL/min Without Inert Material
in the IX compartment of the Ionpure Cell

| Time, min | Amp/Volt | Influent Seawater Flow Rate, mL min$^{-1}$ | Influent DI Flow Rate, mL min$^{-1}$ | Effluent Acidified Seawater pH | Effluent DI Cathode pH |
|---|---|---|---|---|---|
| 20 | 4.70 / 9.40 | 1020 | 120 | 7.59 | - |
| 40 | 4.81 / 9.32 | 1040 | 116 | 7.17 | - |
| 60 | 4.97 / 9.37 | 1040 | 116 | 6.76 | - |
| 80 | 6.08 / 9.02 | 1020 | 118 | 6.31 | - |
| 100 | 6.07 / 8.42 | 1020 | 118 | 6.12 | - |
| 120 | 6.04 / 8.38 | 1000 | 108 | 6.15 | - |

The pH of the effluent acidified seawater was measured for each of the tests in the test series. In Tests 7 and 8, the effluent acidified seawater was collected and 20 mL aliquots were placed in a 1000 mL round bottom flask and degassed using a Brinkmann Roto-Evaporator. A water aspirator provided a vacuum of approximately 15 mm Hg. The carbon dioxide content of each solution was measured by coulometry and plotted as a function of pH, as shown in Figure 4.

In both tests, greater than 98 % carbon dioxide removal was achieved at pHs lower than 4.5. As previously mentioned, $CO_2$ dissolved in water is in equilibrium with $H_2CO_3$ (see Equation 15). The hydration equilibrium constant ($1.70 \times 10^{-3}$) indicates that $H_2CO_3$ is not stable and gaseous $CO_2$ readily dissociates at pH of 4.5, allowing $CO_2$ to be easily removed by degassing. This was observed during all of the experiments.

$CO_2$ in seawater samples of pH of less than 4.5 were naturally and completely degassed upon exiting the acidification cell (exposed to atmosphere during sampling). $CO_2$ content and pH were measured before and after vacuum degassing and there was no significant difference in these two measurements.
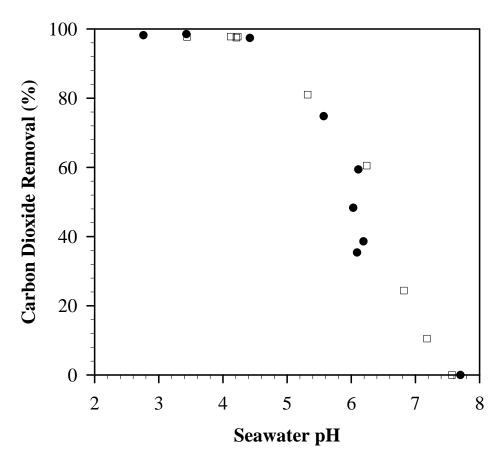
**Figure 4.**     **CO$_2$ Degassed Samples from Test 7 ($\bullet$) and Test 8 ($\square$)**

CO$_2$ in seawater samples of pH greater than 4.5 required assistance by vacuum degassing for complete removal.  In these samples, CO$_2$ content and pH were measured before and after vacuum degassing and there were significant differences in both measurements; CO$_2$ content decreased and pH increased.  Although not quantified, it appeared that level of vacuum degassing required increased as seawater pH increased.

**6.0  CONCLUSIONS**

An electrochemical acidification cell was developed and studied to determine if it could be used as a feasible and practical method for sequestering large quantities of CO$_2$ from seawater.  This indirect path captures bound CO$_2$ in the form of bicarbonate from seawater.  During the experiments the electrolytic regeneration of cation exchange resin, was demonstrated, allowing the simultaneous and continuous ion exchange and regeneration to occur within the cell.  This eliminates the need for regeneration by caustic chemicals that are not ideal for a sea-based application.  The degree of ion exchange and regeneration within the cell was a function of the current applied.  Lowering the pH of seawater by the acidification cell was found to be an electrically driven membrane process, where seawater pH is proportional to applied current and independent of the media contained within the IX compartment.  The studies showed that carbon

dioxide was readily removed from seawater at pHs of less than 6.0. Unassisted and near complete degassing was observed in seawater samples of pH of 5.0 and less. Assisted degassing by vacuum was required in seawater samples at pHs of greater than 5.0. The relationship between seawater bicarbonate concentration, applied current, and seawater pH followed theory with the Key West seawater. The experimental set-up did not allow for recoveries of greater than 95%. It is important to know the upper limit since resources (space and energy) are required to produce a dilute water stream for the electrode compartments.

In addition to carbon dioxide, the cell produced a portion of the hydrogen needed for a hydrocarbon synthesis process with no additional energy penalty. The production of hydrogen gas at the cathode as a byproduct occurred at a predictable rate based on the applied current. Thus the applied current to the cell can be increased to generate more hydrogen gas with no negative performance or operation effects on the acidification cell. The acidification cell's ability to produce a portion of the hydrogen need for the synthesis process would reduce the operational footprint of the whole process, thus making the technology more feasible for a sea-based application.

## 7.0 RECOMMENDATIONS

An electrochemical acidification cell has been developed, tested, and found to be practical for recovering large amounts of $CO_2$ from seawater for use as a carbon feedstock in sea-based fuel production process. It is recommended that this technology be transitioned from the laboratory to a littoral environment where carbon dioxide and hydrogen can be produced in quantities far above those achieved at the laboratory scale. There are many challenges to scaling this technology, including design, ion exchange material regeneration, process efficiency, water fouling, hardness scaling on the cathode, and power requirements that can be assessed and addressed in these future larger scale tests.

## 8.0 ACKNOWLEDGMENTS

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