



NRL/MR/6180--11-9329

Extraction of Carbon Dioxide from Seawater by an Electrochemical Acidification Cell Part II—Laboratory Scaling Studies

HEATHER D. WILLAUER

*Navy Technology Center for Safety and Survivability
Chemistry Division*

FELICE DiMASCIO

*Office of Naval Research
Arlington, Virginia*

DENNIS R. HARDY

*Navy Technology Center for Safety and Survivability
Chemistry Division*

M. KATHLEEN LEWIS

*Office of Naval Research
Arlington, Virginia
and
Luzerne County Community College
Nanticoke, Pennsylvania*

FREDERICK W. WILLIAMS

*Navy Technology Center for Safety and Survivability
Chemistry Division*

April 11, 2011

Approved for public release; distribution is unlimited.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE (DD-MM-YYYY) 11-04-2011		2. REPORT TYPE Memorandum Report		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Extraction of Carbon Dioxide from Seawater by an Electrochemical Acidification Cell Part II—Laboratory Scaling Studies				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Heather D. Willauer, Felice DiMascio,* Dennis R. Hardy, M. Kathleen Lewis,† and Frederick W. Williams				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER 61-9189-0-1-5	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory, Code 6180 4555 Overlook Avenue, SW Washington, DC 20375-5320				8. PERFORMING ORGANIZATION REPORT NUMBER NRL/MR/6180--11-9329	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research One Liberty Center 875 North Randolph Street, Suite 1425 Arlington, VA 22203				10. SPONSOR / MONITOR'S ACRONYM(S) ONR	
				11. SPONSOR / MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES *Office of Naval Research, Arlington, VA †Office of Naval Research, Arlington, VA, and Luzerne County Community College, Nanticoke, PA					
14. ABSTRACT An electrochemical acidification cell has been developed to extract large quantities of carbon dioxide fast and efficiently from seawater. Verification and validation of the electrochemical cell as a function of increased operational time and flow rate using Key West seawater is reported. The electrolytic regeneration of cation exchange resin allowed simultaneous and continuous ion exchange and regeneration to occur within the cell along with control of the seawater pH. At pHs of less than 6.0, carbon dioxide in the seawater was readily removed by vacuum degassing. At higher seawater flow rates, the flow rate to current ratio for a given pH was significantly improved. Prolonged operation of the cell caused the electrical resistance within the cell to increase by 34% signifying scaling on the cathode. These results are significant to the future design of this technology as it is scaled and transitioned to a marine environment.					
15. SUBJECT TERMS Electrochemical acidification cell Seawater pH Carbon dioxide					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Heather D. Willauer
Unclassified	Unclassified	Unclassified	UL	18	19b. TELEPHONE NUMBER (include area code) (202) 767-2673

CONTENTS

1.0	BACKGROUND.....	1
2.0	OBJECTIVE.....	1
3.0	TEST DESCRIPTION.....	1
	3.1 Electrochemical Acidification Cell.....	1
	3.2 Electrochemical Acidification Tests.....	4
4.0	ELECTROCHEMICAL ACIDIFICATION CELL REACTIONS.....	5
5.0	RESULTS AND DISCUSSION.....	6
6.0	CONCLUSIONS.....	13
7.0	RECOMMENDATIONS.....	14
8.0	ACKNOWLEDGEMENTS.....	14
9.0	REFERENCES	14

EXTRACTION OF CARBON DIOXIDE FROM SEAWATER BY AN ELECTROCHEMICAL ACIDIFICATION CELL PART II: LABORATORY SCALING STUDIES

1.0 BACKGROUND

The Naval Research Laboratory (NRL) is developing the chemistry for producing jet fuel from renewable resources in theater [1-5]. The process envisioned would catalytically convert CO₂ and H₂ directly to liquid hydrocarbon fuel in the C₉ – C₁₆ range to be used as JP-5. With such a process the Navy could avoid the risks inherent in procuring fuel from foreign sources and/or maintaining long supply lines. However before a sea-based synthetic fuel process that combines hydrogen produced by nuclear power [6] or solar OTEC [7,8] with CO₂ to make jet fuel at sea can be envisioned, practical, efficient, and economical methods of extracting large quantities of CO₂ and H₂ from seawater must be developed [9-16].

To this end, NRL has made significant advances in the laboratory developing carbon capture technologies [13]. In the summer of 2009 two standard commercially available electrodeionization cells (Nalco Module and Ionpure LX-X Module) were modified to function as electrochemical acidification cells [13]. The objective of those studies was to assess the effects of the acidification cell configuration, seawater composition, flow rate, and current on seawater pH. The data were used to determine the feasibility of this approach for efficiently extracting large quantities of CO₂ from seawater. The studies showed that lowering the pH of the seawater by the acidification cells was an electrically driven membrane process, where pH was proportional to applied current. Carbon dioxide was readily removed from seawater when acidified to a pH of less than 6.0. In addition to carbon dioxide, the cells produced hydrogen gas at the cathode as a byproduct. The hydrogen production could also be controlled by the applied current.

2.0 OBJECTIVE

The initial studies conducted in the summer of 2009 evaluated both synthetic seawater and Key West (KW) seawater. However, the study with KW seawater was only conducted once at an effluent seawater flow rate of 140 mL/min for a period of 23 minutes due to seawater unavailability. Thus the objective of this part II study involved process verification of the electrochemical cell as a function of increased operational time and flow rate using a larger supply of KW seawater.

3.0 TEST DESCRIPTION

3.1 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 attached sulfonic acid groups. The acid functionality provides discrete channels for cations to

migrate through the polymer membrane matrix while blocking the passage of anions when an electrical current is flowing. Figure 1 shows a typical three compartment cell configuration. Based on what was learned in the previous laboratory studies [13], inert ceramic particles were used in the IX compartment to serve as a support structure for the membranes and the electrode compartments were filled with strong cation exchange resin (Rohm & Haas IRA-120).

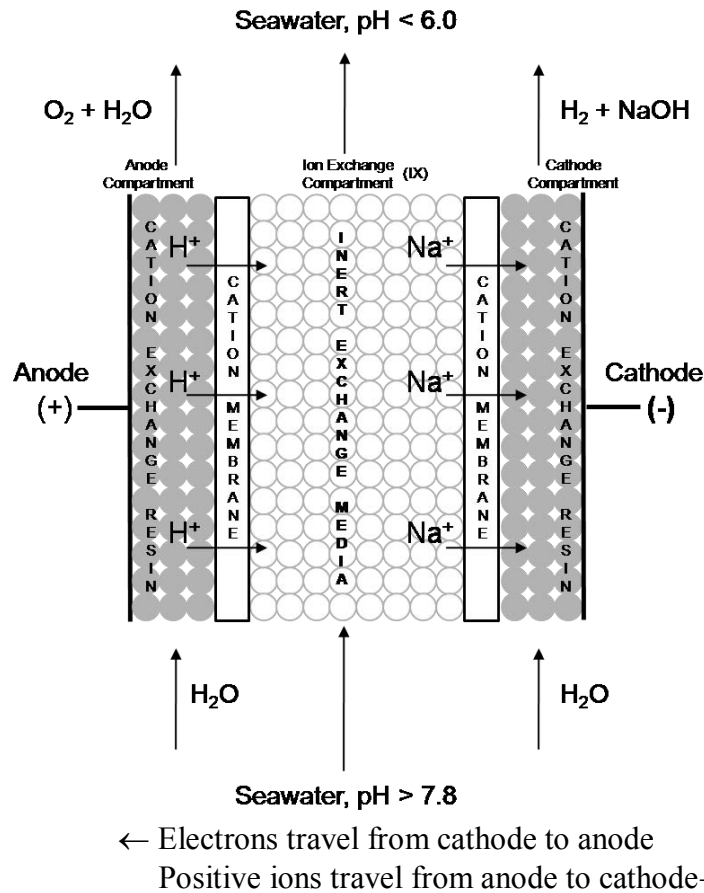


Figure 1. Electrochemical Acidification Cell Schematic Diagram

The acidification cell in Figure 1 used a low electrical current to exchange sodium ions for hydrogen ions in a central stream that was flowing adjacent to two cation exchange membranes. Seawater was passed through the center compartment of the three compartment cell. Sodium ions were transferred through the membrane closest to the cathode and were removed from the seawater by means of direct current (DC) voltage. These sodium ions were 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 was the water fed to the anode compartment. At the anode, H⁺ was 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⁺ in the flowing seawater. Therefore the anolyte must be as dilute as possible, such that H⁺ are in excess and do not compete with any other cations. In this evaluation, deionized water was used as the anolyte.

The catholyte was the water fed to the cathode compartment and it must be free from hardness ions calcium (Ca^{+2}) and magnesium (Mg^{+2}) as previously described [13]. In this evaluation, deionized water was used as the catholyte, so the effect of reverse osmosis (RO) permeate was not evaluated during this feasibility test.

A Nalco module was configured as the electrochemical acidification cell for this evaluation. Table 1 provides a detailed description of the cell's electrical and flow rate specifications along with the materials used in the cell configuration. The anode used in the cell was a dimensionally stable anode (DSA) (mixed precious metal oxide coating on titanium). The flow rate to current ratio required to lower the seawater pH to a target level at flow rates of 140 mL/min and 700 mL/min over a prolonged period will be compared to the previous study that was conducted for 23 minutes at 140 mL/min. This information will be useful for the future design of a larger scale acidification cell, since electrode performance and operating life is based on current density (mA cm^{-2}).

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. IX Flow Rate	20 $\text{cm}^3 \text{s}^{-1}$
Max. Electrolyte Flow Rate	10 $\text{cm}^3 \text{s}^{-1}$
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)

3.2 Electrochemical Acidification Tests

Figure 2 provides a schematic that describes the acidification cell experimental setup. KW 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.

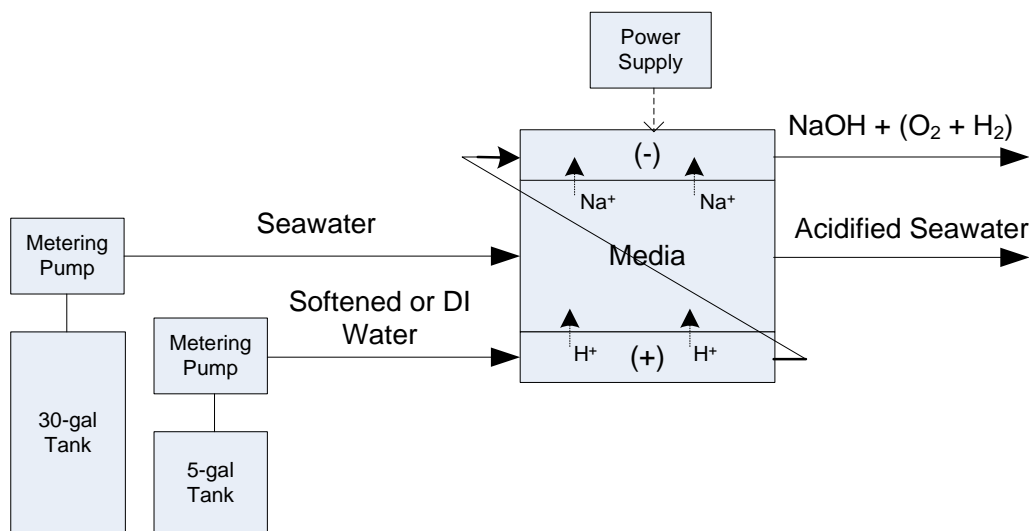


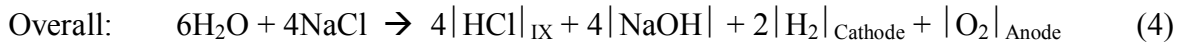
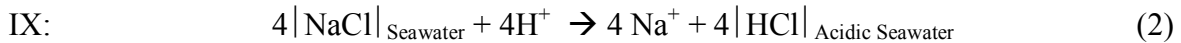
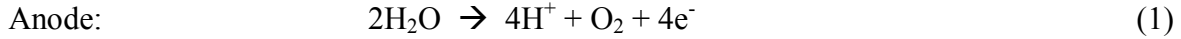
Figure 2. Schematic Showing the Acidification Cell Experimental Layout

Key West seawater was obtained from the Naval Research Laboratory Key West, Florida facility. The pH was 7.6 ± 0.2 and the $[\text{CO}_2]_{\text{T}}$ content was measured to be approximately 100 ppm. The $[\text{CO}_2]_{\text{T}}$ represents the total carbon dioxide concentration in seawater which is defined as the sum of the dissolved bicarbonate and carbonate species along with dissolved gaseous CO_2 . Approximately 75 gallons of seawater was available for the test series. All pH measurements were conducted with a standardized Fisher combination glass electrode. Carbon dioxide contents of solutions were measured by a UIC Coulometric system (UIC Inc, Joliet, IL 60436) [17].

Degassing measurements were made on selective samples from the experiment. For each measurement carbon dioxide was degassed from solution using a Brinkmann Roto-Evaporator. A 10 or 20 mL sample was placed in a 500 mL or 1000 mL round bottom flask and rotated at an rpm setting of 8 for five minutes. A water aspiration provided a vacuum of approximately 2 kPa (15 mm Hg).

4.0 ELECTROCHEMICAL ACIDIFICATION CELL REACTIONS

Previous studies confirmed that the acidification cell shown in Figure 1 operates by exchanging Na^+ for H^+ in a stream that is flowing adjacent to two cation-permeable membranes [13]. 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:



The amount of H^+ generated by the anode 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 $\frac{1}{4}$ mole O_2 gas and 1 mole H^+ and for the cathode reaction, 96,487 A-sec will produce $\frac{1}{2}$ mole H_2 gas and 1 mole OH^- . This allows the theoretical amount of H^+ , OH^- , H_2 , and O_2 produced per amp-second of current passed through the electrodes to be determined:

Anode Reaction

$$\left(\frac{1/4 \text{ mole O}_2}{96,487 \text{ A-sec}}\right)\left(\frac{60 \text{ sec}}{\text{min}}\right) = 0.000155 \frac{\text{mole O}_2}{\text{A-min}} \quad (5)$$

$$\left(\frac{1 \text{ mole H}^+}{96,487 \text{ A-sec}}\right)\left(\frac{60 \text{ sec}}{\text{min}}\right) = 0.000622 \frac{\text{mole H}^+}{\text{A-min}} \quad (6)$$

Cathode Reaction

$$\left(\frac{1/2 \text{ mole H}_2}{96,487 \text{ A-sec}}\right)\left(\frac{60 \text{ sec}}{\text{min}}\right) = 0.000311 \frac{\text{mole H}_2}{\text{A-min}} \quad (7)$$

$$\left(\frac{1 \text{ mole OH}^-}{96,487 \text{ A} \cdot \text{sec}}\right)\left(\frac{60 \text{ sec}}{\text{min}}\right) = 0.000622 \frac{\text{mole OH}^-}{\text{A} \cdot \text{min}} \quad (8)$$

Therefore, seawater with a HCO_3^- concentration of 142 ppm (0.0023 M) and a flow rate of 1 liter per minute, will require a theoretically applied current of 3.70 A to lower the pH to less than 6.0 and convert HCO_3^- to H_2CO_3 .

$$\frac{\left(\frac{0.0023 \text{ mole HCO}_3^-}{\text{Liter}}\right)\left(\frac{1 \text{ Liter}}{\text{min}}\right)}{\left(\frac{0.000622 \text{ mole H}^+}{\text{A} \cdot \text{min}}\right)} = 3.70 \text{ A} \quad (9)$$

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.

The theoretical amount of H_2 gas generated at 3.7 A is

$$\left(\frac{1/2 \text{ mole H}_2}{96,487 \text{ A} \cdot \text{sec}}\right)\left(\frac{60 \text{ sec}}{\text{min}}\right)(3.70\text{A}) = 0.0011 \frac{\text{mole H}_2}{\text{min}} \quad (10)$$

Increasing the current increases the molar ratio of the measured 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 this test series the Nalco cell (Table 1) configuration was such that strong acid cation exchange resin filled the electrode compartments (Figure 1) and inert ceramic particles filled the IX compartment. The electrochemical acidification cell was evaluated at two different sets of flow rate conditions.

In the first set of test conditions, KW seawater passed through the IX compartment at a flow rate of 140 mL/min and dionized water was passed through the electrode compartments at 10 mL/min. These test conditions were identical to those run previously in the Initial Feasibility I test using KW seawater [13]. Table 2 summarizes the results of the first test in the series. In the previous test series 0.47 amps brought the seawater pH below 6. When the same current was applied to the cell in this test series, the pH was lowered from 7.8 to 6.11. As the current to the cell was increased further to 0.52, the pH of the effluent seawater unexpectedly increased. Table 2 shows that the pH of the effluent seawater remained above 6 as the current was increased from

0.47 to 1.0 amps over a period of 90 minutes. After 105 minutes the pH fell to 5.22 at an applied current of 1.25 amps. Thus indicating less current was needed to lower the pH of the effluent seawater further. The flow rate to current ratio when the pH was lowered to 6.04 was estimated to be 140 mL/min/1.0 amps = 140 mL/min-Amp (Table 2 Data)

This ratio is significantly lower than the theoretical ratio of 267 calculated for similar conditions as described in equation 9 (3.7 amps theoretical minimum) as:

$$1000 \text{ mL/min}/3.70 \text{ amps} = 140 \text{ mL/min}/X$$

$$X = 0.525 \text{ Amps}$$

Theoretical Ratio: $140 \text{ mL/min}/0.518 \text{ amps} = 270 \text{ mL/min-Amp}$

and inconsistent with the previous study in which the flow rate to current ratio when the seawater pH was lowered below 6 was 298 (140 mL/0.47 amps).

Table 2. Acidification of KW 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
Initial Feasibility Studies II (1st Test)				
15	0.47/4.81	140	10	6.11
30	0.48/4.79	140	10	7.07
45	0.52/4.84	140	10	6.96
60	0.58/5.11	140	10	7.01
75	0.69/5.57	140	10	6.59
90	1.00/6.73	140	10	6.04
105	1.25/7.51	140	10	5.22
120	1.14/6.91	140	10	4.66
135	0.94/6.22	140	10	4.96

The operational behavior of the cell may be explained by the equilibrium conditions of the ion exchange material in the cell's electrode compartments at the beginning of the test series. The cell had been stored in deionized water after the Initial Feasibility Studies I test series for a period of six months. When the cell was initially stored, the cation exchange resin was in the hydrogen form in the anode compartment and in the sodium form in the cathode compartment (Figure 1). During the six months of storage, the ions migrated within the cell. A portion of the cation exchange resin in the anode compartment converted to the sodium form while some of the cation exchange resin in the cathode compartment converted to the hydrogen form. Since the

amount of H^+ ions generated from the oxidation of water on the anode is proportional to the applied electrical current, the higher current during the first 90 minutes of the test forced regeneration of the ion exchange material in the electrode compartments. The H^+ ions generated at the anode exchanged on the resin and released Na^+ ions. The Na^+ ions then migrated through the cation exchange membrane and into the IX compartment. The migrating Na^+ ions passed through the cation exchange membrane at the cathode and exchanged on the resin to convert all the resin in that compartment to the sodium form. Table 2 shows that after 90 minutes the ion exchange material in electrode compartments was regenerated, allowing more H^+ ions to pass through the membrane closest to the anode to acidify the seawater. As a result, the current and pH of the effluent seawater dropped and the cell began functioning as anticipated.

Table 3. Acidification of KW 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
Initial Feasibility Studies II (2nd Test)				
15	0.49 / 4.61	140	10	5.62
30	0.49 / 4.62	140	10	5.71
45	0.59 / 4.99	140	10	5.49
60	0.68 / 5.39	140	10	5.15
75	0.79 / 5.77	140	10	4.37
90	0.73 / 5.53	140	10	4.68
105	0.75 / 5.66	140	10	4.32
Initial Feasibility Studies I				
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

Table 3 is the start of the second test in the Initial Feasibility II series. The Table shows that when 0.49 amps of current were applied to the cell for 15 minutes, the pH of the effluent seawater was lowered from 7.70 to 5.62. The pH stabilized to 5.71 after an additional 15 minutes at the same applied current of 0.49 amps. The flow rate to current ratio when the pH was 5.71 was estimated to be 287 (140 mL/min/0.49 amps). This ratio is very similar to the theoretical ratio of 267 and consistent with the Initial Feasibility Studies I study in which the flow rate to current ratio when the seawater pH was lowered from 7.60 to 5.97 was 298 (140 mL/0.47 amps). As the current was increased further over 15 minute intervals the pH of the effluent seawater continued to decrease. The experiment was conducted for a total of 105 minutes.

Figure 3 is a plot of the applied current in amps as a function of effluent acidified KW seawater pH for both Feasibility studies shown in Table 3. The results in Figure 3 and Table 3 confirm that the cell was operating similarly to the previous test series once the ion exchange equilibrium conditions were re-established in the cell. The results demonstrate that lowering of the seawater pH was an electrically driven membrane process, where seawater pH was proportional to the applied current.

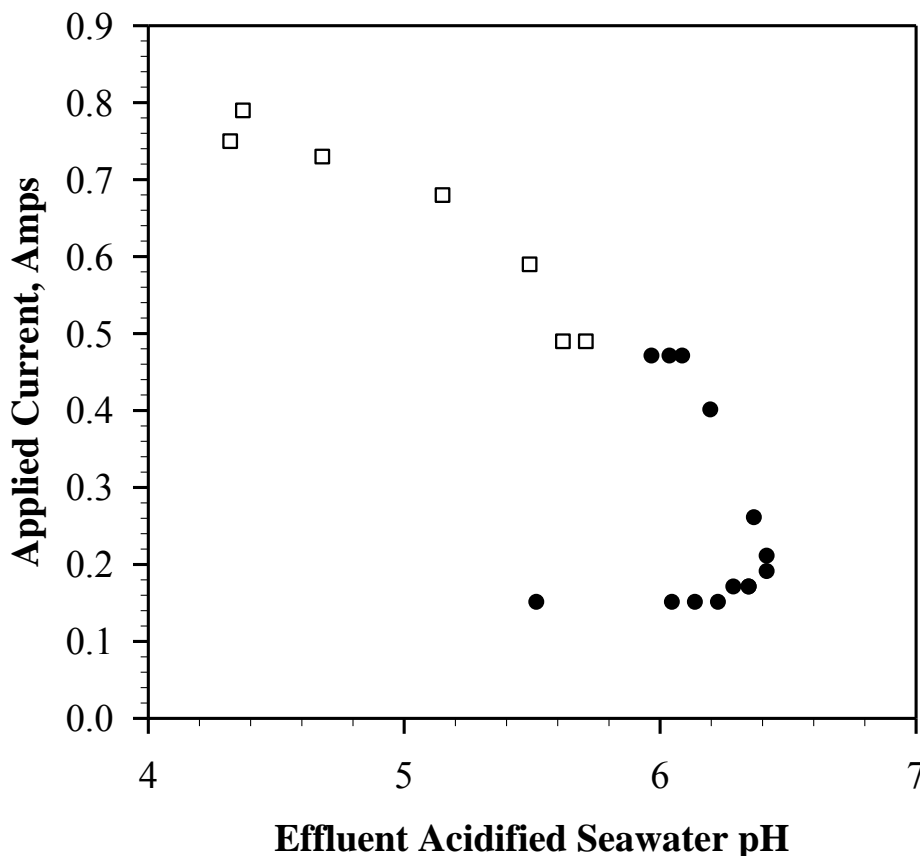


Figure 3. KW seawater acidification by electrochemical acidification cell: (●) Feasibility Test I and (□) Feasibility Test II.

In the third test, KW seawater was used to determine the effect that flow rate through the IX compartment had on the performance of the Nalco cell. KW seawater was pumped at 700 mL/min and maintained for 135 minutes. The results summarized in Table 4 also include an additional test that was conducted for the purposes of collecting samples for degassing experiments. Table 4 confirms that at higher flow rates the pH of the effluent seawater can be lowered using the acidification cell. In addition, the results suggest that the flow rate to current ratio for a given pH under higher flow rate conditions was significantly improved and the recovery was at 93%. The term “recovery” is used to define the ratio of product quantity (influent seawater flow rate, Table 4) over the total feed quantity to the cell (influent seawater flow rate and influent dionized flow rate, Table 4) 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 pre-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 in future scaled experiments.

Table 4. Acidification of KW seawater at 700 mL/min

Time, min	Amp/Volt	Influent Seawater Flow Rate, mL min⁻¹	Influent DI Flow Rate, mL min⁻¹	Effluent Acidified Seawater pH
Initial Feasibility Studies II (3rd Test)				
15	3.75/15.62	690	49	4.27
30	3.70/15.76	680	50	4.21
45	3.65/16.43	700	50	4.18
60	3.50/16.82	700	50	4.14
75	3.01/15.76	700	50	4.78
90	3.10/16.57	700	50	4.65
105	3.10/17.01	700	50	4.51
120	3.10/17.37	700	50	4.30
135	2.34/14.34	700	50	5.34
Degassing Experiments				
15	2.25/14.5	700	50	5.37

Figure 4 is a plot of electrical resistance (voltage divide by amperage) as a function of time for the second and third tests. When the cell was operated at 140 mL/min of seawater to the IX compartment, the electrical resistance initially decreased over time. After 75 minutes the Figure shows the electrical resistance began to increase slightly. This trend continued in the next test series as the KW seawater flow rate was increased from 140 mL/min to 700 mL/min. A 34% increase in the electrical resistance from 4.07 to 6.13 ohms over the course of the higher flow rate experiment was a sign of hardness scaling on the cathode. Scaling (mineral deposits) takes place at the high-pH surface of the cathode. The formation of mineral deposits increases the electrical resistance (voltage divided by amperage) of the module and could cause a pressure drop in the cathode compartment. This in turn leads to a reduction in current efficiencies.

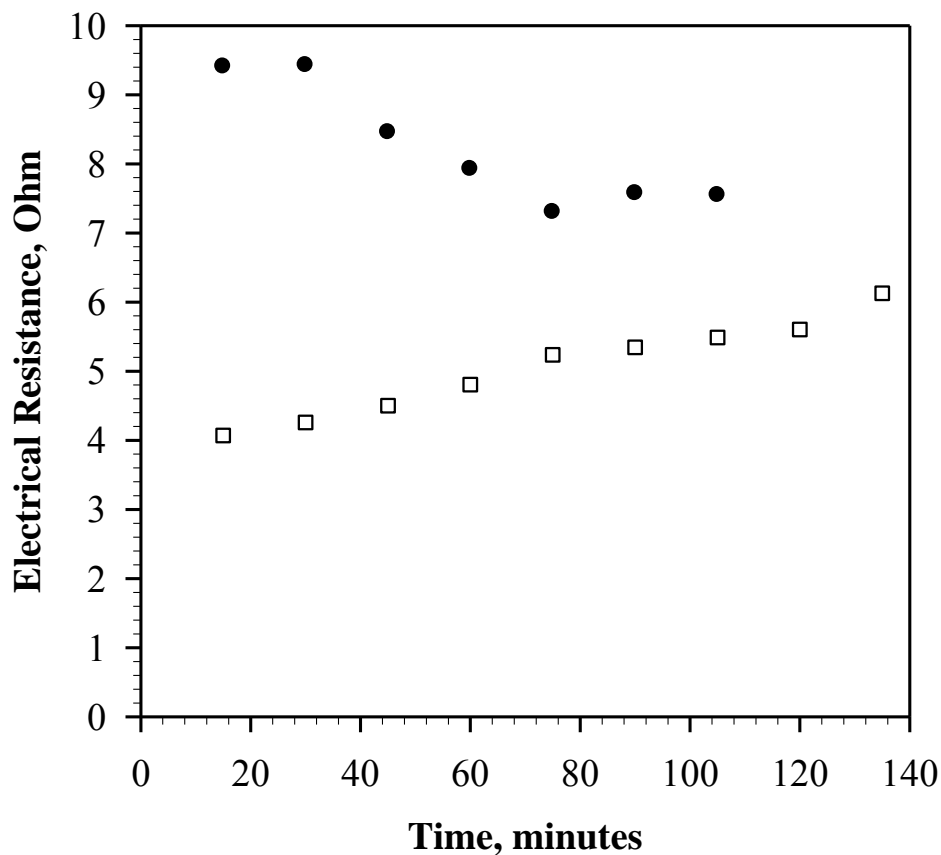


Figure 4. Electrical resistance as a function of time for two different sets of electrochemical acidification cell flow rate conditions: (●) 140 mL/min and (□) 700 mL/min.

Since deionized water was the catholyte fed to the cathode compartment, hardness ions must have been introduced to the cathode from the IX compartment. Hardness ions in seawater include calcium (Ca^{+2}) and magnesium (Mg^{+2}) ions, with a total concentration of less than 2,000 mg/L. It was initially thought there would be a negligible likelihood of hardness ions migrating from the IX to the cathode compartment for the following reasons: First, the amount of cations that needed to be exchanged to lower the pH of the seawater was less than 0.5% of the total cations present in the seawater. Second, the molar ratio of Na^{+} ions to Ca^{+2} and Mg^{+2} was approximately 7 to 1. Finally, the mobility coefficients of the ions favor Na^{+} ($50.1 \text{ cm}^2 \Omega^{-1} \text{ eq}^{-1}$) over $1/2\text{Ca}^{+2}$ ($59.5 \text{ cm}^2 \Omega^{-1} \text{ eq}^{-1}$) and $1/2\text{Mg}^{+2}$ ($53.0 \text{ cm}^2 \Omega^{-1} \text{ eq}^{-1}$).

In future scaled experiments, the acidification cell will be designed so that the polarity of the cell can be reversed. Cyclically reversing the polarity of the cell's electrodes will reduce the mineral deposits on the electrode that is operating as the cathode. The change in polarity causes the minerals (scaling) and organics to disassociate from the electrode surface. This is a common

practice in Electrodialysis Reversal (EDR) process to desalinate brackish ground and surface waters [18].

Table 5. CO₂ Degassed Samples from Acidification of KW seawater at 700 mL/min

Seawater	Seawater (pH)	Vacuum Exposure Time (minutes)	CO ₂ Content (mg/mL)	Reduction (%)
Initial Seawater Content	7.79	0	0.100	0
Effluent Seawater Table 4 time 60 minutes	4.14	0	0.070	30
Effluent Seawater Table 4 time 60 minutes	4.14	5	0.010	90
Effluent Seawater Table 4 flow rate conditions	5.37	5	0.021	79
Effluent Seawater Table 4 flow rate conditions	5.37	5	0.001	99
Effluent Seawater Table 4 flow rate conditions	5.37	2.5	0.002	98
Effluent Seawater Table 4 flow rate conditions	5.37	1	0.002	98
Effluent Seawater Table 4 flow rate conditions	5.37	0.5	0.002	98

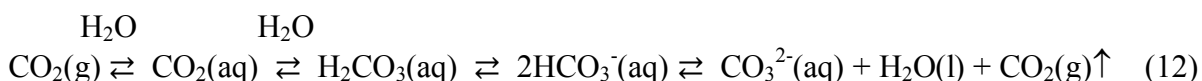
In the previous test series conducted at seawater flow rates of 140 mL/min, greater than 98% carbon dioxide in the seawater samples at a pH of less than 4.5 were spontaneously degassed upon exiting the acidification cell (exposed to atmosphere during sampling). When CO₂ is dissolved in seawater it is in equilibrium with H₂CO₃ as shown in Equation 11



The hydration equilibrium constant (1.70×10^{-3}) indicates that H₂CO₃ is not stable and gaseous CO₂ readily dissociates at pH of 4.5, allowing CO₂ to be easily removed by degassing. In efforts to substantiate this principle at higher seawater flow rates, effluent acidified seawater samples having a pH of 4.14 (Table 4) were collected and 20 mL aliquot solutions were placed in a 1000 mL round bottom flask and degassed for 5 minutes using a Brinkmann Roto-Evaporator. The carbon dioxide content of the seawater before and after vacuum degassing was measured by coulometry and the results are given in Table 5.

The initial CO₂ concentration of KW seawater was approximately 0.100 mg/mL which corresponds to 0.0023 moles/L. After the seawater solution was acidified to pH 4.1, the CO₂ content of the seawater measured 0.070 mg/mL, thus indicating the solution was naturally degassed by 30% upon exiting the acidification cell (exposed to the atmosphere during

sampling). When a vacuum was applied to an effluent sample for 5 minutes, the CO₂ content was reduced to 0.01 mg/mL and 90% degassing was achieved. The loss in natural degassing of CO₂ from seawater as it exited the acidification cell may be attributed to the higher seawater flow rate conditions and the larger volume of seawater exiting the cell. Under these conditions, the seawater has less time to physically degas. Longer exposure to the atmosphere would result in competing phenomena as the seawater buffer in equation 12 struggles to re-equilibrate with the atmosphere, possibly resulting in the uptake of CO₂ back into the seawater solution. However as CO₂ is spontaneously degassing, the solubility of CO₂ back into the seawater decreases.



The results of the previous test series also illustrated that CO₂ in seawater samples having a pH less than 6.0 and greater than 4.5 required assistance by vacuum degassing for complete CO₂ removal. Preliminary studies to determine the effects of sample volume and applied vacuum time on degassing effluent seawater having a pH of 5.37 are provided in Table 5. After a 20 mL seawater sample was degassed for 5 minutes, 79% of the CO₂ content was removed. Reducing the sample volume to 10 mL and the round bottom flask to 500 mL resulted in a 99% removal of CO₂. When individual 10 mL effluent seawater samples were degassed over four different applied vacuum time intervals, complete degassing was observed. These results confirm that at higher acidification seawater flow rates, the effluent KW seawater can be degassed at pHs lower than 6. However, the results indicate that under higher flow rate conditions sample volume and applied vacuum conditions may be extremely relevant to the future scaling of the system for purposes of producing large quantities of CO₂ as feedstock for synthetic jet fuel production.

6.0 CONCLUSIONS

An electrochemical acidification cell has been developed and tested as a function of increased operational time and flow rate using KW seawater. KW seawater simulates sample conditions that will be encountered in an actual ocean process for recovering CO₂. This indirect path captures bound CO₂ in the form of bicarbonate from seawater. During the initial experiments sufficient current was needed to electrolytically regenerate the ion exchange materials in the cathode and anode compartments after the cell had been stored in deionized water for a period of six months. Once the ion exchange materials were regenerated within the acidification cell, the seawater pH was proportional to applied current. Thus the results at seawater flow rates of 140 mL/min were consistent with the previous test series. At higher seawater flow rates, the flow rate to current ratio for a given pH was significantly improved. However after prolonged operational times the electrical resistance increased by 34% signifying scaling on the cathode. The scaling resulted from the seawater hardness ions calcium (Ca⁺²) and magnesium (Mg⁺²) migrating from the IX compartment.

Degassing studies showed that carbon dioxide was readily removed from seawater at a pH less than 6.0. However at higher seawater flow rates, assisted degassing by vacuum was required.

The results suggested that sample volume and applied vacuum conditions may be relevant as the acidification cell is scaled to handle higher seawater flow rate conditions in the future.

7.0 RECOMMENDATIONS

An electrochemical acidification cell has been developed, tested, and found to be practical for recovering large amounts of CO₂ 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 marine environment where carbon dioxide and hydrogen can be produced in quantities 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

This work was supported by the Office of Naval Research both directly and through the Naval Research Laboratory.

9.0 REFERENCES

- [1] Dorner, R. W.; Hardy, D. R.; Williams, F. W.; Davis, B. H.; Willauer, H. D. Influence of Gas Feed Composition and Pressure on the Catalytic Conversion of CO₂ Using a Traditional Cobalt-Based Fischer-Tropsch Catalyst. *Energy & Fuels*, 2009, 23, 4190.
- [2] Dorner, R. W.; Willauer, H. D.; Hardy, D. R.; Williams, F. W. "Effects of Loading and Doping on Iron-based CO₂ Hydrogenation Catalyst," Memorandum Report 6180-09-9200; Naval Research Laboratory: Washington DC, August 24, 2009.
- [3] Dorner, R. W.; Hardy, D. R.; Williams, F. W.; Davis, B. H.; Willauer, H. D. K and Mn doped Iron-based CO₂ Hydrogenation Catalysts: Detection of KAlH₄ as part of the catalyst's active phase. *Applied Catalysis A-General*, 2010, 373, 112.
- [4] Dorner, R. W.; Hardy, D. R.; Williams, F. W.; Davis, B. H.; Willauer, H. D. Effects of Ceria-doping on a CO₂ Hydrogenation Iron-Manganese Catalyst, *Catalysis Communications*, 2010, 11, 816.
- [5] Dorner, R. W.; Hardy, D. R.; Williams, F. W.; Davis, B. H.; Willauer, H. D. Heterogeneous catalytic CO₂ conversion to value-added hydrocarbons, *Energy and Environmental Science*, 2010, 3, 884.
- [6] Schultz, K. Bogart, S. L. Noceti, R. P.; Cugini, A. V. Synthesis of Hydrocarbon Fuels Using Renewable and Nuclear Energy. *Nuclear Technology* 2009, 166, 56.
- [7] Mohanasundaram, S. Renewable Power Generation-Utilising Thermal Energy From Oceans. *Enviro. Sci. & Eng.* 2007, 4, 35.

- [8] Avery, W. H.; Wu, C. *Renewable Energy From The Ocean*; Oxford University Press: New York, 1994.
- [9] Hardy, D. R. Zagrobelny, M.; Willauer, H. D.; Williams, F. W. "Extraction of Carbon Dioxide From Seawater by Ion Exchange Resin Part I: Using a Strong Acid Cation Exchange Resin" Memorandum Report 6180-07-9044; Naval Research Laboratory: Washington DC, April 20, 2007.
- [10] Willauer, H. D.; Hardy, D. R.; Lewis, M. K.; Ndubizu, E. C.; Williams, F. W. Recovery of CO₂ from Aqueous Bicarbonate Using a Gas Permeable Membrane. *Energy & Fuels*, 2009, 23, 1770.
- [11] Willauer, H. D.; Hardy, D. R.; Lewis, M. K.; Ndubizu, E. C.; Williams, F. W. "Recovery of [CO₂]_T from Aqueous Bicarbonate Using a Gas Permeable Membrane" Memorandum Report 6180-08-9129; Naval Research Laboratory: Washington DC, June 25, 2008.
- [12] Willauer, H. D.; Hardy, D. R.; Lewis, M. K.; Ndubizu, E. C.; Williams, F. W. "Extraction of CO₂ From Seawater By Ion Exchange Resin Part II: Using a Strong Base Anion Exchange Resins" Memorandum Report 6180-09-9211; Naval Research Laboratory: Washington DC, September 29, 2009.
- [13] DiMascio, F.; Willauer, H. D.; Hardy, D. R.; Lewis, M. K.; Williams, F. W. "Extraction of Carbon Dioxide from Seawater by an Electrochemical Acidification Cell Part I: Initial Feasibility Studies" Memorandum Report 6180-10-9274; Naval Research Laboratory: Washington DC, July 23, 2010.
- [14] Willauer, H. D.; Hardy, D. R.; Williams, F. W. "The Feasibility and Progress of Scaling NRL Technologies for Producing Jet Fuel at Sea Using Carbon Dioxide and Hydrogen" Memorandum Report 6180-10-9300; Naval Research Laboratory: Washington DC, September 29, 2010.
- [15] Willauer, H. D.; Hardy, D. R.; Lewis, K. M.; Ndubizu, E. C.; Williams, F. W. "The Effects of Pressure on the Recovery of CO₂ by Phase Transition from a Seawater System by Means of Multi-layer Gas Permeable Membranes." *J. Phys. Chem. A*, 2010, 114, 4003.
- [16] Hardy, D. R. "Sea-based Fuel Synthesis Work at NRL from FY02 to FY07 (October 2001-October 2006)" Memorandum Report 6180-10-9276; Naval Research Laboratory: Washington DC, August 5, 2010.
- [17] Johnson, K. M., King, A. E., Sieburth, J. Coulometric TCO₂ Analyses for Marine Studies: An Introduction. *Marine Chem.* 1985, 16, 61.
- [18] Dermentzis, D. Continuous Electrodeionization through Electrostatic Shielding *Electrochimica Acta* 2008, 53, 2953.

